

Comparison of historical violins by non-destructive MRI depth profiling

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ABSTRACT

The back plates of master violins at the Ashmolean Museum in Oxford and the Museo del Violino in Cremona were analyzed by portable magnetic resonance imaging with the NMR-MOUSE in terms of depth profiles. Distributions of transverse NMR relaxation times were recorded versus depth at points of small curvature across the violin back plates providing insight into the physical states of the materials. Their analysis reveals the effects of surface treatments, wood treatment, and possible wood degradation. While conclusions about the type of treatment cannot be drawn, the profiles report surprising differences between the violins from the museums in Oxford and Cremona.

1. Introduction

The art of making today's violins is largely defined by the violin makers of Cremona beginning in the first half of the 16th century [1,2]. The most valuable violins have been fabricated by the Stradivari, Amati and Guarneri workshops between the second half of the sixteenth century and the first half of the eighteenth century. In addition to the selection of wood, the geometry, the design and the fine craftsmanship, their unsurpassed quality of sound is often linked to the type of wood treatment, in particular, the different layers of ground and varnish [3–5]. Depending on the varnish its application has been shown to enhance the elastic modulus corresponding to the stiffness of the wood in the affected surface layers [6]. On the other hand, wear and aging of varnish and wood as well as restoration procedures during the use and life of a violin also affect the sound quality and leave their signatures in the material properties of the instrument [1,4,7]. Like any other material, also the wood of musical instruments ages [8]. There are long-term irreversible effects and short term, largely reversible effects. The reversible effects concern the deformation upon tuning and the deformation due to the impact of changing humidity. Moisture affects the hydrogen bonds connecting the hemicellulose of the wood to the lignin, so that deformation and ambient humidity are coupled on the time scale of hours leading to mechano-sorptive creep to which an instrument is exposed during concerts, practice and travel [8–10]. Longtime

irreversible aging results from biological attack by fungus and from fatigue due to extended vibrational load which breaks down the amorphous hemicellulose molecules linking the mostly rigid crystalline cellulose and the lignin [11,12].

Non-destructive analyses of violin materials often focus on analyzing the composition and thickness of the varnish and ground layers [13–20], and the way they affect the sound properties while the state of the wood and how its material properties are affected by age, use, maintenance and restoration are more difficult to characterize non-destructively [8–10]. This is believed to be a consequence of the fact, that common non-destructive analytical techniques like ultra-violet (UV) induced fluorescence, optical coherence tomography (OCT), and infrared (IR) reflectance spectroscopy are surface techniques, which typically can penetrate only up to 100 µm of the instrument surface [13,19], while 3D techniques with larger fields of view like neutron imaging (NI) [21] and micro-computer tomography (µCT) [20,22,23] primarily provide dimensional and density information, even though NI is also sensitive to moisture and resins [23] and CT to glue [22,24], and, in principle, to crystallinity. NI, in particular, is demanding and expensive to execute. On the other hand, magnetic resonance imaging (MRI) is capable of providing information on material properties non-destructively albeit at inferior resolution limited to about 50 µm [25,26]. So far it has not been applied to a systematic analysis of violins.

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By ^{13}C NMR spectroscopy and elemental analysis of wood samples from four Stradivari instruments and one Guarneri instrument, Tai et al. found that about one-third of the hemicellulose had decomposed after three centuries, and that there were indications of lignin oxidation and reduced equilibrium moisture content. Furthermore, they observed the presence of Al, Ca, Cu, Na, K, and Zn [27]. On the other hand, by NMR and synchrotron X-ray diffraction studies the same authors found, that the crystallinity of cellulose had remained intact, along with the adhesion between holocellulose and lignin. They point out that, in addition to high-frequency vibrations over time, some of the hemicellulose breakdown could have been initially promoted by heat treatments or changes in pH, and that possibly the increased concentration of divalent and trivalent metal ions could crosslink carbohydrate and lignin chains to compensate for reduced molecular adhesion. The authors conclude, that today the maple wood in Stradivari violins has properties very different from their modern counterparts, and postulate that these arise from the combined effects of aging, chemical treatment, and vibration.

Our study corroborates the physical aspects of these findings from a *destructive* analysis with an analysis of distributions of NMR relaxation times measured *non-destructively* across the maple back plates of 15 precious violins at the Ashmolean Museum in Oxford and the Museo del Violino in Cremona. A comparative non-destructive analysis of a selected set of violins from Cremona by OCT, XRF, FT-IR spectroscopy and NMR depth profiling has recently been published [28]. The work reported below places the focus on non-destructive NMR depth profiling across the full thickness of the backplates. To compare the violins from the Oxford and the Cremona collections directly through the lens of NMR, the complete set of depth profiles measured from the violins of both collections is reported. This includes a subset of the Cremona profiles discussed in [28] to compare different analytical surface techniques. The compilation of all NMR depth profiles through the maple back plates reveals striking differences between the instruments housed at the two sites. Their existence is highlighted in a unique way. Their origin cannot be explained by the NMR measurements alone and warrants further studies by different techniques to correlate these findings with the individual histories of these instruments.

2. Materials and methods

2.1. Materials

NMR depth profiles were measured through the maple back plates of 15 violins from the Hill collection at the Ashmolean Museum in Oxford and from the collection at the Museo del Violino in Cremona (Table 1). The Hill collection at the Ashmolean Museum started with a

gift of a group of instruments from the firm W.E. Hill & Sons in 1939 and was subsequently enlarged by gifts mostly from other members of the Hill family [29,30]. The firm was founded in 1880 by William Ebsworth Hill, the great-great-grandson of the first violin maker in the family, Joseph Hill (1715–1784). It had quickly reached an outstanding reputation in making, restoring and selling stringed instruments. As the Hills realized more and more the damage done to these instruments by constant playing and repeated restoration, they eventually decided to donate some of their own instruments to a museum in an effort to preserve them from further harm [29,30]. Thus, the mission of the Hill collection is to preserve rare instruments in their original state.

The violin collection in Cremona was started in 1961 with the acquisition of the Joachim violin made by Antonio Stradivari (1644–1737) in 1715 by the town of Cremona from Desmond Hill of London [31]. This violin was renamed to ‘Cremonese’ and became the crown jewel of the growing Cremona collection. The collection was first housed in the Town Hall along with a significant heritage of original tools of the Stradivari family acquired in 1920, and subsequently moved to the Museo del Violino in 2013. The mission of the Museo del Violino in Cremona is only somewhat different from that of the Ashmolean Museum, in that scientific research on the historical violins is encouraged, and some of the violins can be played on occasion in musical performances [31] under supervision of a strict monitoring plan to optimize their conservation by studying the varnishes, wood and structures before and after a performance [32]. In contrast to the Ashmolean Museum, the Museo del Violino holds both a public collection from the Municipality of Cremona and violins from private owners, the so-called Friends of Stradivari. Therefore, the history of the Cremona violins and their state of conservation can be more heterogeneous than that of the violins in the Hill collection.

One depth profile was acquired for each violin of the Hill collection in Oxford at a spot near the position of the least curvature in the center (Fig. 1a) except for one spot near the side. Up to three depth profiles were acquired for each violin in Cremona at spots selected according to the thickness of the varnish and low curvature [28]. A subset of these profiles has been discussed in [28] with the focus on a comparison of different nondestructive techniques for stratigraphic analyses of ancient Cremonese violins. In addition to the violins, untreated and recently treated maple wood samples (*acer pseudoplatanus*) were investigated in view of the signature of wood treatment on the NMR signal. An exemplary result is reported in the supporting information to [28]. The focus of this work is on comparing two sets of violins, one set with more homogeneous histories of the individual violins and the other with more heterogeneous histories by means of their wood signatures as revealed by NMR profiles across the entire depth of the violin backs.

2.2. NMR measurements

Profiles through the depths of the back plates were measured with the Magritek NMR-MOUSE (Nuclear Magnetic Resonance – MOBILE Universal Surface Explorer) [33–35] in a point-by-point fashion at a nominal resolution of 100 μm (Fig. 1a). Details of the NMR instrumentation along with an analysis of the spatial resolution are reported in the supplementary information. With it, depth profiles can be measured through layered structures following the principles of Magnetic Resonance Imaging (MRI) [25,26]. The hydrogen NMR signal is collected from a flat sensitive slice outside the scanner at a fixed distance of 2 to 25 mm away from the surface, depending on the particular type of NMR-MOUSE and the operating parameters. In this study, depth profiles were measured with a PM5 NMR-MOUSE from Magritek. The sensitive slice of this device is 5 mm away from the surface of the sensor, and its dimensions are 10 mm \times 12 mm. To acquire depth profiles, the instrument is set up so that the sensitive slice is aligned parallel to the object layers and positioned inside the object (Fig. 1a). The NMR signal is then collected point by point by increasing the distance between the object and the scanner in a stepwise fashion between

Table 1
Violins investigated by NMR depth profiling.

Year	Manufacturer	Name of violin / provenance	Location
1564	Andrea Amati	Charles IX	Oxford
1618	Antonio and Girolamo Amati		Oxford
1646	Nicola Amati	On loan from Pamela Rosenfeld	Oxford
1649	Nicola Amati	Alard	Oxford
1658	Nicola Amati	Hämmerle	Cremona
1672	Jakob Stainer		Oxford
1679	Antonio Stradivari	Hellier	Cremona
1683	Antonio Stradivari	Cipriani Potter	Oxford
1696	Francesco Ruggeri		Oxford
1700	Edward Pamphilon		Oxford
1715	Antonio Stradivari	Cremonese	Cremona
1722	Antonio Stradivari	Rode, on loan from the Segelman trust	Oxford
1734	Giuseppe Guarneri del Gesù	Principe Doria	Cremona
1793	Lorenzo Storioni	Bracco	Cremona
1816	Nicolas Lupot		Oxford

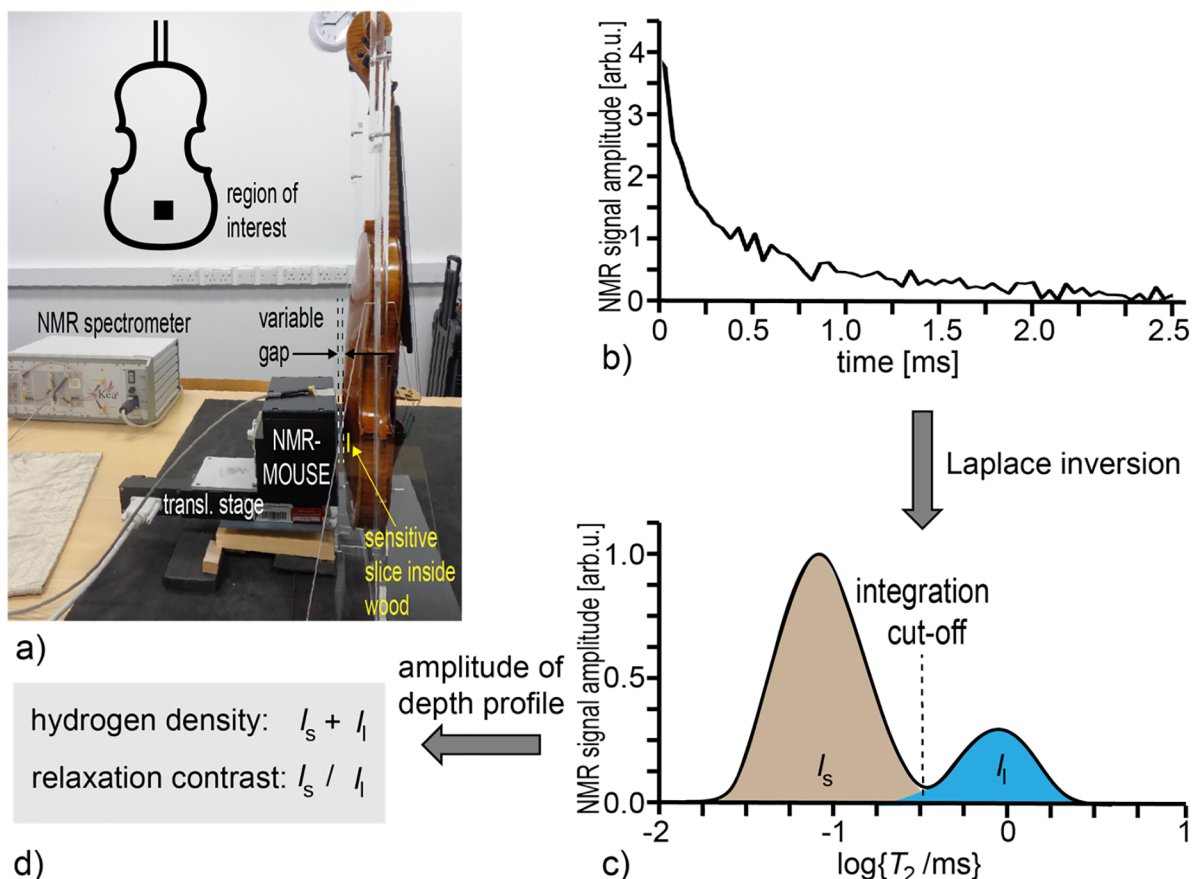


Fig. 1. Measurement and data processing. a) Experimental setup at the Ashmolean Museum. b) Typical NMR relaxation decay from a violin back plate. c) Relaxation-time distribution obtained from (b) by inverse Laplace analysis and definition of peak integrals. d) Definitions of hydrogen density and relaxation contrast from the peak integrals I_s and I_l .

measurements under computer control, whereby the scanner is mounted on a precision translational stage. There are many applications of the NMR-MOUSE to non-destructive materials testing. These concern not only the analysis and characterization of technical materials and consumer products like food stuffs, polymer products, car tires, biological materials, and porous media [35–38] but also heritage objects such as books, easel paintings, painted walls, and mummies [37,39–43].

The nominal spatial resolution of a depth profile is set by the slice width and the step size of the translational stage for a flat stratigraphy. Violins are curved objects. The impact of the measurement parameters and the curvature on the spatial resolution is analyzed in the supplement, showing that the structures thinner than about 0.2 mm are not resolved in this study. The amplitude of the profile is derived from the acquired NMR signal in a variety of ways. By default, the transverse relaxation decay is measured for protons, the nuclei of hydrogen (^1H), with a multi-echo sequence following Carr, Purcell, Meiboom, and Gill as a function of time (Fig. 1b) [37,38]. The total amplitude of this signal reports the average apparent hydrogen density in the volume of the sensitive slice. The relaxation decay can be decomposed into a sum of exponential functions that decay with characteristic NMR relaxation times T_2 by algorithms referred to as inverse Laplace transformation (Fig. 1c). NMR relaxation times scale with molecular mobility. The signal with short T_2 originates from molecules with restricted mobility, and the signal with long T_2 from mobile molecules. The molecular mobility impacts many macroscopic properties like viscosity, modulus of elasticity, and stiffness. An energetically stiff material has low molecular mobility and short transverse relaxation time T_2 .

The Laplace inversion of signal decays acquired as a function of depth produces depth-resolved distributions of relaxation times T_2 on a

logarithmic scale. The measurement of such distributions as a function of the sensor position is well established in the oil well-logging industry. There, they characterize rock porosity and fluid type from borehole walls with NMR well-logging instruments, which are inserted into the borehole and follow similar measurements principles as the NMR-MOUSE [44]. But the step size for well logging is on the order of meters, while for the violin measurements reported here it is 0.1 mm.

NMR relaxation-time distributions are a valuable information source for material properties. In the NMR signal from maple wood recorded with the NMR-MOUSE at short echo time (Fig. 1c), one typically finds two relaxation peaks, one at short T_2 (near 0.09 ms) and one at long T_2 (near 1 ms). The one at short T_2 is attributed to the protons from amorphous cellulose and hemicellulose in the wood matrix and the one at long T_2 to bound water [45]. Their numeric peak integrals are denoted by I_s and I_l , respectively. Depending on the state of the wood and the wood treatment, the positions and peak intensities in the relaxation-time distribution vary.

The information contained in the peaks of the relaxation-time distributions can be condensed in different ways to produce signal amplitudes in one-dimensional NMR depth profiles (Fig. 1d) [37]. For maple wood, the integral of the complete relaxation-time distribution is given by the sum $I_s + I_l$ of the two peak integrals. It corresponds to the total amplitude of the NMR signal (Fig. 1b) and scales with the total number of hydrogen nuclei detected in the sensitive slice. Apart from the signal lost during the deadtime of the sensor, the sum is proportional to the hydrogen density. This apparent hydrogen density is henceforth referred to simply as hydrogen density. On the other hand, the ratio I_s/I_l of the peak integrals (Fig. 1d) reports material stiffness or brittleness from lower bound water content and possibly shifts in the wood relaxation signal to shorter times [28]. On account of the average

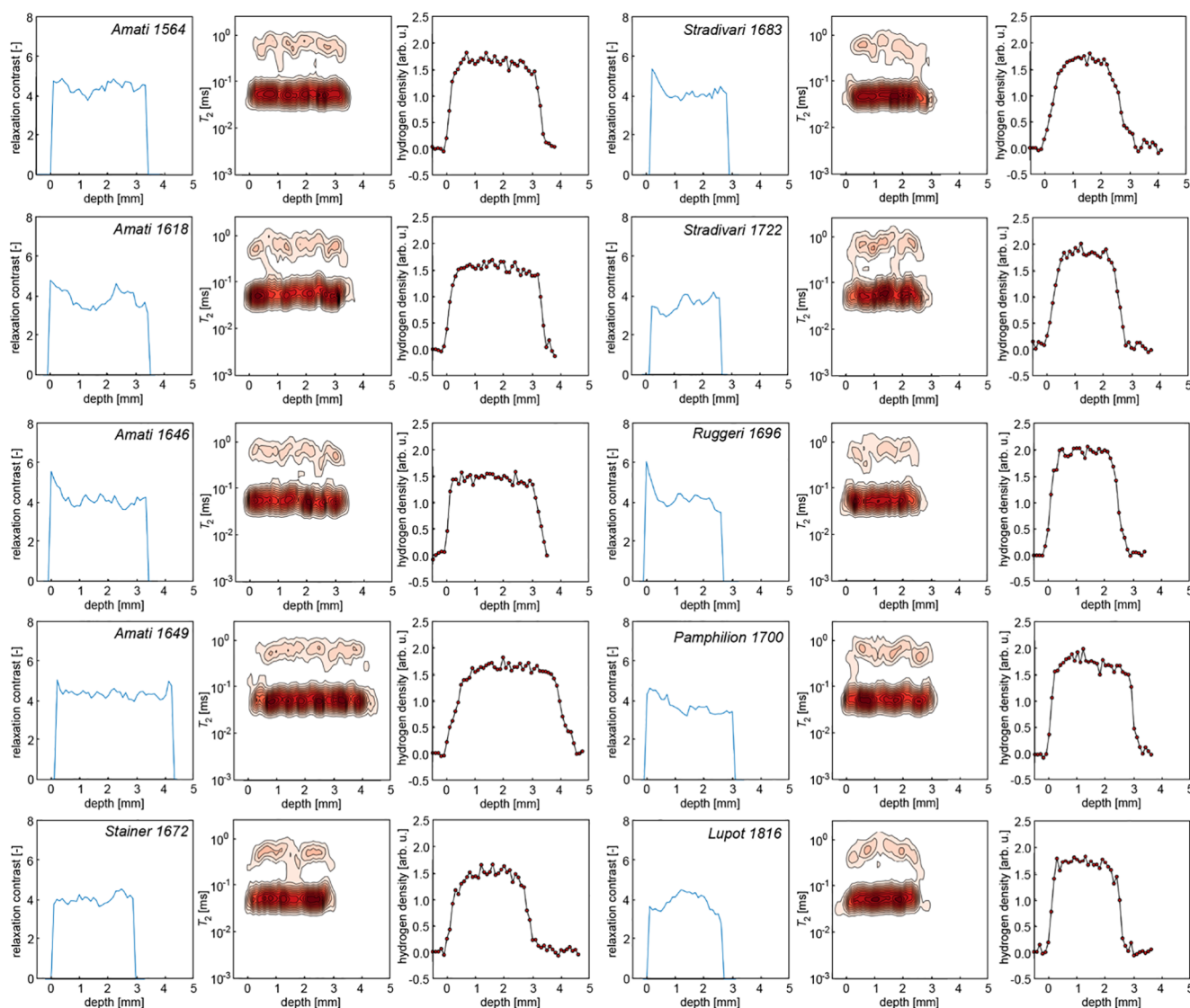


Fig. 2. Depth profiles through the maple backs of violins from the Hill Collection in the Ashmolean Museum, Oxford, measured at points of small curvature mostly near the bottom center (cf. Fig. 1a). Three depth profiles are shown for each violin derived from one measurement. Left: Relaxation contrast corresponding to wood stiffness. Middle: Distributions of T_2 relaxation times. Right: Hydrogen density corresponding to wood density.

divide between both relaxation peaks, all relaxation-time distributions in this study were evaluated by calculating the ratio I_s/I_l from the integrals of the distributions from $1\ \mu\text{s}$ to $210\ \mu\text{s}$ and $230\ \mu\text{s}$ to $2\ \text{ms}$ (Fig. 1c). This ratio is called relaxation contrast. Depth profiles of the relaxation contrast revealed layer structures across the violin back plates, which are invisible in hydrogen-density profiles, whereby higher relaxation contrast indicates stiffer material, and lower contrast indicates softer material.

3. Comparison of depth profiles from the Cremona and Oxford violins

Depth profiles through the back plates of ten violins from the Hill collection dating from 1564 (Andrea Amati) to 1816 (Nicolas Lupot) were scanned in Ashmolean Museum, Oxford (Table 1, Fig. 2). Overall the profiles are inconspicuous and reveal a mostly well conserved state of the wood judging by a representative depth profile such as that from the Amati 1564 violin. The hydrogen density (right) reports constant wood density across the plate, and so does the relaxation contrast (left) with a constant high value above 4 corresponding to wood stiffness. A similar, constant and high value for the wood stiffness is only found for

the Amati 1649. In view of the residual measurement noise, the variations of the peak positions and amplitudes at long relaxation time ($T_2 = 1\ \text{ms}$) and short relaxation time ($T_2 = 0.09\ \text{ms}$) in the depth-resolved relaxation-time distribution (middle) of the Amati 1564 are insignificant across the back plate and report constant bound water content and state of the wood matrix, very similar to the Amati 1649.

Taking the similar depth profiles of the Amati 1564 and the Amati 1649 for reference, it is noted, that the hydrogen-density profiles of all violins in Fig. 5 are essentially constant and first of all report different thickness of the wooden plates at the spots measured. The typical value of the hydrogen density is near 1.5 for all Amati violins and the Stainer 1672. Higher values are found for the other violins (Stradivari 1683, Stradivari 1722, Ruggeri 1696, Pamphillon 1700, Lupot 1816), whereby the Ruggeri 1696 has a value close to 2, even higher than the value of the Stradivari 1722. These higher values can arise from a different selection of the particular wood or from some form of wood treatment.

The relaxation contrast parameter I_s/I_l varies more from violin to violin than the hydrogen density $I_s + I_l$. While for the recent maple wood samples (Fig. SM3 in [28]) the relaxation contrast varies between 3 and 4 (a) or 2 and 3 (b,c), it is about 4 and higher for most of the

Oxford violins (Fig. 2, left for each violin). This indicates, that the bound water content is lower in the older wood of the violins than in the recent maple wood sample, or, less likely, that the amount of amorphous cellulose has increased by degradation of the undetectable amount of crystalline cellulose. The net effect is that the violin wood has an NMR signature that reports a higher stiffness than that of the recent maple wood sample. Moreover, peaks in the relaxation-contrast parameter are noted at the position of the outer surface at zero depth for the Amati 1646, the Stradivari 1683, and the Ruggeri 1696, which extend to values of up to 6. These peaks are similar in appearance to the peaks of the surface-treated maple-wood sample (Fig. SM3c in [28]) and suggest the existence of some surface treatment which enhances the strength of the wood in a surface layer. Although the surface treatments of violins are well known [5], knowing their NMR signature is helpful in identifying treatments of hidden surfaces, i.e. the inside surfaces. Due to the low depth resolution of the measurement, the thickness of this surface layer cannot be quantified better than by stating that it is less than 0.2 mm as detailed in the [supplementary information](#).

The Lupot 1816 is the only violin from that set, which has been found to have lower stiffness at the inner and outer surfaces of the back plate than in the interior (Fig. 2, bottom right). Here the bound-water peak in the relaxation-time distribution is shifted to lower relaxation times at the outer and the inner surfaces. The convex appearance of the peak position across the thickness of the back plate suggests some yet to be determined type of treatment not only of the outer surface but also of the inner surface.

Comparing the depth profiles of the ten violins from the Hill collection in Oxford (Fig. 2) to those measured at different spots for five violins at the Museo del Violino in Cremona (Fig. 3) [28] dating from 1658 (Amati Hämmerle) to 1793 (Storioni Il Bracco), reveals striking differences between the two sets. The depth-resolved relaxation-time distributions appear wrinkled in comparison with the straight peak positions across depth observed for most violins from the Hill collection. Also, the hydrogen-density profiles vary more across depth and between different spots of one violin back. The value of 1.5 found for the Amati violins in the Hill collection is essentially only found for the Guarneri del Gesù 1734 at one (black) out of three points and the Stradivari 1715 for two out of three points (black, red) across the entire thickness of the back plate. The Storioni 1793 is an interesting case. The back plate seems to be divided into an inner and an outer layer of roughly the same thickness. While the inner layer exhibits the reference value of 1.5 for the hydrogen density, the outer layer has a higher value except at the point of low varnish (red). At the points of medium and more varnish, the hydrogen density exhibits an elevated value possibly due to some type of past wood treatment from the outside. A similar division of the hydrogen density between inner and outer sides of the backplate is found in one out of two spots for the Amati 1658 (red) and the Guarneri del Gesù 1734 (red). Other profiles show lower hydrogen density, in particular, the Stradivari 1679 at two spots (red, blue) and the Guarneri del Gesù 1734 (blue). A strikingly low and oddly shaped hydrogen-density profile has been measured for the Amati 1658 at one (black) of two spots measured. Unfortunately, this measurement could not be repeated, so that it is not clear, if the measurement was flawed. Nevertheless, for future record, the data are included in this overview.

The relaxation-contrast profiles of the Cremona violins vary greatly. They show values between 3 and 7 whereas apart from surface treatments the value is about 4 for most of the Oxford violins. For the Storioni 1793, the Guarneri del Gesù 1734 and the Stradivari 1679 these profiles also differ between the three measurement spots at each violin. This is not so for the Stradivari 1715, where very similar profiles have been recorded for all three measurement spots across the length of the back plate. This violin shows a strong peak at the outer surface and a smaller one at the inner surface, suggesting that also the inner surface has been treated with some formulation that enhances the stiffness of the material. Also, different from the rather narrow peaks in the relaxation contrast parameter profiles of the Stradivari 1683 and the

Ruggeri 1696 in Oxford, some peaks can be as broad as 1 mm although with amplitude changes similar to the hypothesized surface treatments of the Oxford violins, for example for the inside of the Storioni 1793 (blue) and the Stradivari 1679 (black) in Cremona. To clarify the origin of these variations further studies are needed. One may speculate that these variations in wood stiffness result from the wood itself, from manufacturing and restoration procedures, while in principle they can also come from extended vibrational strain.

The most striking difference between the depth profiles through the backs of the Oxford and Cremona violins is noted in the depth-resolved relaxation-time distributions. Here the Stradivari 1715 (red and black) and the Amati 1658 (red) are prominent examples for unusual variations of relaxation-time distributions across the thickness of the maple backs. For the Amati 1658 (red) the relaxation signal of the wood matrix has shifted to significantly longer relaxation times across a range of more than 1 mm from the outer surface. For the Stradivari 1715 (black and red) the wood relaxation signal is shifted to longer relaxation times only in the center of the back plate but not at the outer and inner surfaces. A shift to longer relaxation times indicates a change in the wood structure to more mobility on the molecular scale, which can result from degradation of the amorphous cellulose molecules into smaller fragments with higher mobility, for example, by fungal attack or by mechanical fatigue from vibration. If it is chemical degradation, then it should start at the surface in agreement with the profile of the Amati 1658 (red). But since the relaxation peaks of the Stradivari 1715 (black and red) near the inner and outer surfaces appear in the range of healthy wood, one may hypothesize that the chemically degraded cellulose has been stabilized by some surface or wood treatment. This is in agreement with the shift of the amorphous cellulose signal to shorter relaxation times observed near the surface of the maple-wood sample treated with ground and varnish [28].

4. Summary and conclusions

Fifteen violins of exceptional craftsmanship have been analyzed in total at the Ashmolean Museum in Oxford and the Museo del Violino in Cremona, in terms of depth profiles through their backs by portable MRI. The measurement principle follows the one established in the well-logging industry by recording NMR relaxation-time distributions from different spots along some stretch of the object and analyzing them for material properties. For the violins, these distributions have been measured across the thickness of the maple backs with a step size of 0.1 mm and analyzed for the hydrogen density corresponding mostly to wood density and the relaxation contrast parameter which reveals the material stiffness. Both parameter profiles as well as the depth-resolved relaxation-time distributions differ considerably between the violins investigated in Oxford and those in Cremona. While the profiles of the violins studied from the Hill collection are inconspicuously straight and report mostly pristine wood apart from the signature of outer surface treatments in some cases, the profiles from the analyzed Cremona violins are wrinkled, bearing the signature of surface treatments, degradation of amorphous cellulose and treatments not only of the outer but also of the inner surfaces. These observations are in line with the more heterogeneous past of the Cremona violins, coming from different owners and histories. The early insights of the Hill generations of violin makers and the opportunity to house the Hill collection in the Ashmolean museum since 19th century at similar conditions of conservation appear to have left their signature in a higher homogeneity of the wood of the violins studied in Oxford. Moreover, this non-invasive study of physical violin-wood properties corroborates the recent results of Tai et al. obtained invasively [28] on the differences of Stradivari maple compared to contemporary maple being due to chemical aging and vibrational fatigue. Making use of the non-invasive character of the NMR-depth profiling methodology demonstrated here, a variety of follow-up studies can be perceived to further understand the various mechanisms and fabrication processes which convert a tree into a

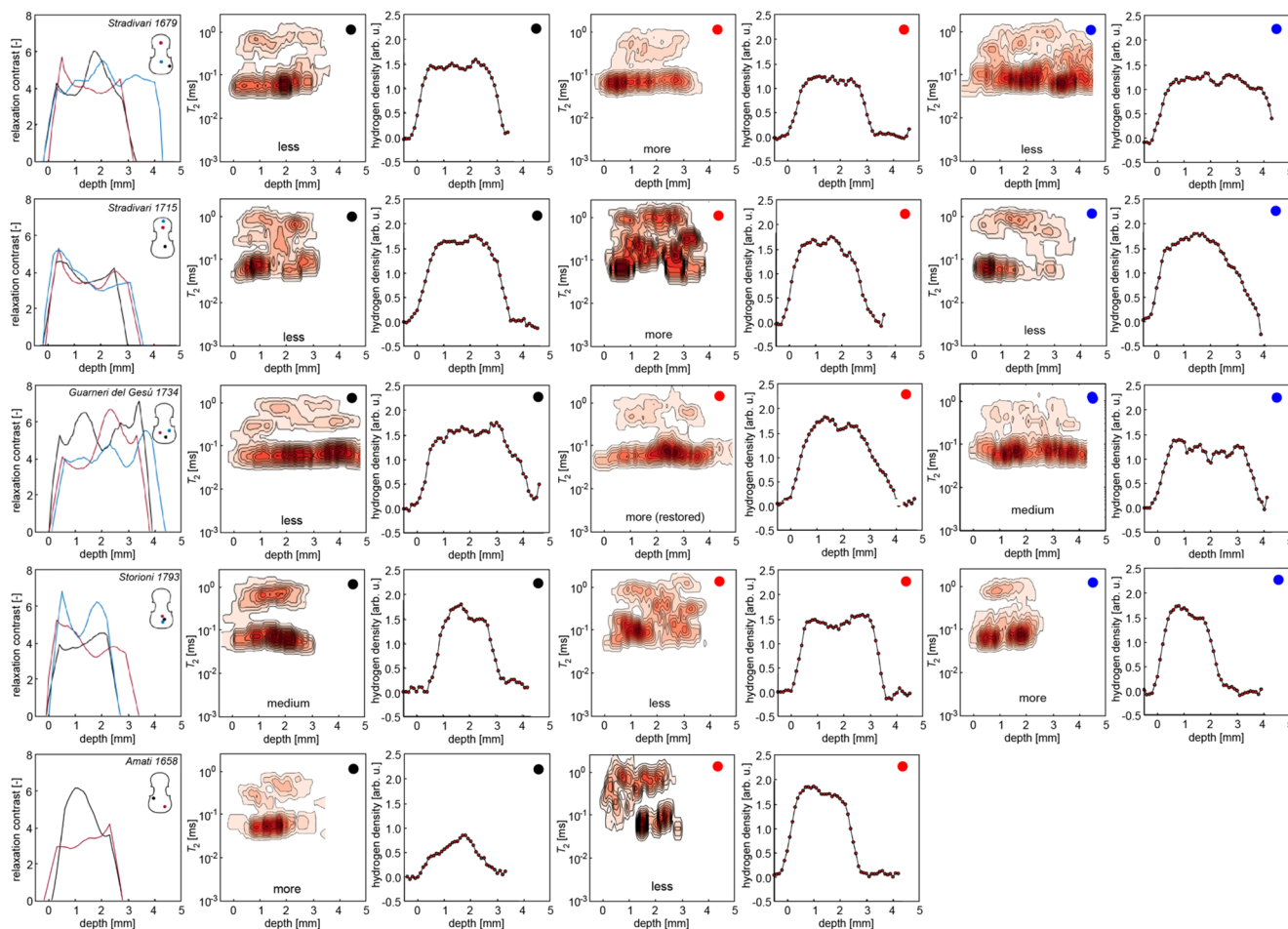


Fig. 3. Complete set of all measured NMR depth profiles through the maple backs of violins from the collection at the Museo del Violino in Cremona measured at two to three different spots for each violin. Three depth profiles are shown for each spot derived from one measurement. They are relaxation-contrast profiles, distributions of T_2 relaxation times and hydrogen density. The measurement positions were chosen according to the thickness of the varnish and are color coded. The annotations 'more', 'medium', 'less' refer to the varnish thickness at the measurement spot [28].

master violin as well as the different processes of aging and the impact of restoration. In this way the NMR depth-profiling methodology may assist in improving conservation and restoration strategies of such instruments.

Declaration of competing interest

BB is on the board of directors of Magritek Ltd. Else, the authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the reported work.

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Data availability

The data sets generated during analysis in the current study are

available from the corresponding author on reasonable request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2020.105219>.

References

- [1] W. Kolneder, Das Buch der Violine, Atlantis Musikbuch-Verlag, Mainz, 1972, 1993.
- [2] K. Roy, *The violin: its history and making*, International Violin Company, Baltimore, 2006.
- [3] F. Setragno, M. Zanoni, F. Antonacci, A. Sarti, M. Malagodi, T. Rovetta, C. Invernizzi, Feature-based analysis of the impact of ground coat and varnish on violin tone qualities, *Acta Acust.* United Ac. 103 (2017) 80–93, <https://doi.org/10.3813/AAA.919035>.
- [4] J.-P. Echard, L. Bertrand, A. von Bohlen, A.-S. Le Hô, C. Paris, L. Bellot-Gurlet, B. Soulier, A. Lattuat-Derieux, S. Thao, L. Robinet, B. Lavédrine, S. Vaiedelich, The nature of the extraordinary finish of stradivari's instruments, *Angew. Chem. Int. Ed.* 49 (2010) 197–201, <https://doi.org/10.1002/anie.200905131>.
- [5] B. Brandmair, P.S. Greiner, *Stradivari Varnish*, B. Brandmair, Munich, 2010.
- [6] S.L. Lämmlein, D. Mannes, B.V. Damme, I. Burgert, F.W.M. Schwarze, Influence of varnishing on the vibro-mechanical properties of wood used for violins, *J. Mat. Sci.* 54 (2019) 8063–8095, <https://doi.org/10.1007/s10853-019-03440-9>.
- [7] R. Rovetta, C. Invernizzi, G. Fiocco, M. Albano, M. Licelli, M. Gulmini, A. Alf, F. Fabbri, A.G. Rombolà, M. Malagodi, The case of Antonio Stradivari ex-San Lorenzo violin: history, restorations and conservation perspectives, *J. Arch. Sci.: Rep.* 23 (2019) 443–1350.
- [8] M. Fioravanti, Conservation of historical wooden musical instruments: advance in understanding material aging, *Music in Art* 39 (2014) 311–316.
- [9] M. Fioravanti, G. Goli, B. Carlson, Viscoelastic and mechano-sorptive studies

- applied to the conservation of historical violins: a case study of the Guarneri “del Gesù” violin (1743) known as the “Cannone”, *J. Cult. Heritage* 14 (2013) 297–330.
- [10] G. Goli, B. Marcon, L. Busoni, B. Carlson, A. Cavalli, A. Giordano, P. Mazzanti, P. Montanari, M. Togni, M. Fioravanti, Antique violins: effect of the player on the moisture content, *Int. J. Conservation Sci.* 8 (2017) 177–186.
 - [11] D.G. Hunt, E. Balsan, Why old fiddles sound sweeter, *Nature* 379 (1996) 681, <https://doi.org/10.1038/379681a0>.
 - [12] H. Akahoshi, S. Chen, E. Obataya, Effects of Continuous Vibration on the Dynamic Viscoelastic Properties of Wood, *Proc. Effects of Playing on Early and Modern Musical Instruments*, Royal College of Music, London, September 9–10, 2015, pp. 65–67.
 - [13] G. Fiocco, T. Rovetta, C. Invernizzi, M. Albano, M. Malagodi, M. Licchelli, A. Re, A.L. Giudice, G.N. Lanzafame, F. Zanini, M. Iwanicka, P. Targowski, M. Gulmini, A micro-tomographic insight into the coating systems of historical bowed string instruments, *Coatings* 9 (2019) 81, <https://doi.org/10.3390/coatings9020081>.
 - [14] C. Invernizzi, G.V. Fichera, M. Licchelli, M. Malagodi, A non-invasive stratigraphic study by reflection FT-IR spectroscopy and UV-induced fluorescence technique: the case of historical violins, *Microchem. J.* 138 (2018) 273–281.
 - [15] T. Rovetta, C. Invernizzi, M. Licchelli, F. Cacciatori, M. Malagodi, The elemental composition of Stradivari’s musical instruments: new results through non-invasive EDXRF analysis, *X-Ray Spectrom.* 47 (2018) 159–170.
 - [16] P. Dondi, L. Lombardi, C. Invernizzi, T. Rovetta, M. Malagodi, M. Licchelli, Automatic analysis of UV induced fluorescence imagery of historical violins, *JOCCH* 10 (2017) 1–12.
 - [17] C. Invernizzi, A. Daveri, M. Vagnini, M. Malagodi, Non-invasive identification of organic materials in historical stringed musical instruments by reflection infrared spectroscopy: a methodological approach, *Anal. Bioanal. Chem.* 409 (2017) 3281–3288.
 - [18] C. Daher, L. Drieu, L. Bellot-Gurlet, A. Percot, C. Paris, A.-S. Le Hô, Combined approach of FT-Raman, SERS and IR micro-ATR spectroscopies to enlighten ancient technologies of painted and varnished works of art, *J. Raman Spectrosc.* 45 (2014) 1207–1214.
 - [19] C. Invernizzi, A. Daveri, T. Rovetta, M. Vagnini, M. Licchelli, F. Cacciatori, M. Malagodi, A multianalytical non-invasive approach to violin materials: the case of Antonio Stradivari “Hellier” (1679), *Microchem. J.* 124 (2016) 743–750, <https://doi.org/10.1016/j.microc.2015.10.016>.
 - [20] G. Fiocco, T. Rovetta, M. Malagodi, M. Licchelli, M. Gulmini, G. Lanzafame, F. Zanini, A.L. Giudice, A. Re, Synchrotron radiation micro-computed tomography for the investigation of finishing treatments in historical bowed string instruments: issues and perspectives, *Eur. Phys. J. Plus* 133 (2018) 525, <https://doi.org/10.1140/epjp/i2018-12366-5>.
 - [21] E.H. Lehmann, S. Lämmerlein, D. Mannes, Neutron imaging as tool for investigations on historical musical instruments, *J. Arch. Sci.: Rep.* 20 (2018) 239–243.
 - [22] S.A. Sirr, J.R. Waddle, CT analysis of bowed stringed instruments, *Radiology* 204 (1997) 801–805.
 - [23] E.H. Lehmann, D. Mannes, Wood investigations by means of radiation transmission techniques, *J. Cult. Herit.* 13S (2012) S35–S43.
 - [24] B.C. Stael, T.M. Bowman, A comparison of wood density between classical cremonese and modern violins, *PLoS ONE* 3 (2008) e2554.
 - [25] P.T. Callaghan, *Magnetic Resonance Microscopy*, Clarendon Press, Oxford, 1991.
 - [26] B. Blümich, *NMR Imaging of Materials*, Clarendon Press, Oxford, 2000.
 - [27] H.-C. Tai, G.-C. Li, S.-J. Huang, C.-R. Jhu, J.-H. Chung, B.Y. Wang, C.-S. Hsu, B. Brandmair, D.-T. Chung, H.M. Chen, J.C.C. Chan, Chemical distinctions between Stradivari’s maple and modern tonewood, *PNAS* 114 (2017) 27–32.
 - [28] C. Invernizzi, G. Fiocco, M. Iwanicka, M. Kowalska, P. Targowski, B. Blümich, C. Rehorn, V. Gabrielli, D. Bersani, M. Licchelli, M. Malagodi, Non-invasive mobile technology to study the stratigraphy of ancient Cremonese violins: OCT, NMR-MOUSE, XRF and reflection FT-IR spectroscopy, *Microchem. J.* 155 (2020) 104754.
 - [29] J. Whiteley, *Stringed Instruments: Viols, Violins, Citterns, and Guitars in the Ashmolean Museum*, Ashmolean Museum, Oxford, 2008.
 - [30] J. Milnes (Ed.), *Musical Instruments in the Ashmolean Museum: The Complete Collection*, Oxford Musical Instrument Publishing, Berkhamsted, 2011.
 - [31] F. Cacciatori, *Lo Scrigno dei Tesori*, Edizione Museo del Violino, Cremona, 2014.
 - [32] G.V. Fichera, M. Albano, G. Fiocco, C. Invernizzi, M. Licchelli, M. Malagodi, T. Rovetta, Innovative monitoring plan for the preventive conservation of historical musical instruments, *Stud. Conserv.* 63 (2018) S531–S534.
 - [33] www.magritek.com.
 - [34] G. Eidmann, R. Savelsberg, P. Blümmler, B. Blümich, The NMR MOUSE, a Mobile Universal Surface Explorer, *J. Magn. Reson., Ser. A* 122 (1) (1996) 104–109, <https://doi.org/10.1006/jmra.1996.0185>.
 - [35] F. Casanova, J. Perlo, B. Blümich, *Single-Sided NMR*, Springer, Berlin, 2011.
 - [36] B. Blümich, F. Casanova, J. Perlo, Mobile single-sided NMR, *Prog. Nucl. Magn. Reson. Spectr.* 52 (2008) 197–269.
 - [37] B. Blümich, S. Haber-Pohlmeier, W. Zia, *Compact NMR*, de Gruyter, Berlin, 2014.
 - [38] B. Blümich, *Essential NMR*, second ed., Springer-Nature, Cham, 2019.
 - [39] D. Capitani, V. Di Tullio, N. Proietti, Nuclear magnetic resonance to characterize and monitor cultural heritage, *Prog. Nucl. Magn. Reson. Spectr.* 64 (2012) 29–69.
 - [40] B. Blümich, F. Casanova, J. Perlo, F. Presciutti, C. Anselmi, B. Doherty, Noninvasive testing of art and cultural heritage by mobile NMR, *Acc. Chem. Res.* 43 (2010) 761–770.
 - [41] M. Baías, B. Blümich, Nondestructive Testing of Objects from Cultural Heritage with NMR, in: G. Webb (Ed.), *Modern Magnetic Resonance*, Springer, Cham, 2018. doi:10.1007/978-3-319-28275-6_29-1.
 - [42] C. Rehorn, B. Blümich, Cultural heritage studies with mobile NMR, *Angew. Chem. Int. Ed.* 57 (2018) 7304–7312.
 - [43] F. Rühli, T. Böni, J. Perlo, F. Casanova, M. Baías, E. Egarter, B. Blümich, Non-invasive spatial tissue discrimination in ancient mummies and bones in situ by portable nuclear magnetic resonance, *J. Cultural Heritage* 8 (2007) 257–263.
 - [44] G.R. Coates, L. Xiao, M.G. Prammer, *NMR Logging Principles and Applications*, Halliburton Energy Services, Houston, 1999.
 - [45] E.L. Lindh, C. Terenzi, L. Salme, I. Furo, Water in cellulose: evidence and identification of immobile and mobile adsorbed phases by ^2H MAS NMR, *PCCP* 19 (2017) 4360–4369.