Chemical and Microstructural studies of violins

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Experimental studies on the fabric of old violins have involved a range of microscopical techniques (light microscopy, scanning electron microscopy) and chemical analysis (e.g. X-ray analysis in association with electron microsopy). The microscopy yields information about the structure and nature of the wood (e.g. details of cell structures and whether there are signs of damage or degradation), and information about surface layers and coatings. The chemical analysis provides data on the nature of such surface layers and coatings, but may also show whether the wood has been treated chemically in any way.

What do the results tell us?

Questions we might be interested in answering include learning about techniques used to make the instruments, which may be of interest to luthiers and conservators. More controversially, we might try to discover whether the sound quality of the instruments can be correlated with observations.
In this article, examples will be given of a number of different observations, and their relevance to current practices will be discussed.

I I Overview of experimental techniques

I.1 Microscopical techniques

The simplest way of gaining information about microstructures is to use a single lens, which might be in the form of a magnifying glass or a jeweller's loupe typically magnifying no more than 15x. Even this is enough to reveal something of the cell structure of wood. The ultimate example of a single lens is due to van Leeuwenhoek, working in Delft at the end of the 17th century. He was able to achieve magnifications of up to about 400x, and to show detail of organisms and natural materials which had never been seen before. These sorts of magnifications from a single lens are exceptional, though, and for ordinary purposes multiple lenses which together form a light microscope are required. These microscopes can be used in reflection (revealing surface structures, or interiors of transparent materials), or transmission (typically of very thin sections of materials such as wood which would not normally be transparent). The techniques are capable of providing sophisticated analysis, which can reveal information about crystal structures as well as topographical detail. Optical microscopy suffers the limitation that the higher the magnification the smaller the depth of field, so that at high magnifications samples have to be very flat and smooth for appreciable sized regions to be in focus at once. The greatest magnification which can be achieved by optical light microscopes is determined by the limitation that features smaller than the wavelength of light cannot be resolved.

For higher magnifications, shorter wavelength radiation is needed, and this can be achieved using fast electrons which have been accelerated by high voltages. The most accessible type of electron microscopy is Scanning Electron Microscopy, SEM. A narrow beam of electrons is raster scanned across the sample. At each point the electrons are reflected or not, and an appropriate signal is generated. A magnified image is created by rastering this signal as light on a screen. Transmission Electron Microscopy, TEM, is experimentally much more difficult (sample preparation and examination, and image interpretation are all problematic), although higher magnifications and resolutions can be obtained.

These techniques are summarised and compared in Table 1.

Technique	Advantages	Limitations
Light microscopy	Accessible, can be relatively inexpensive. Colour information retained Some crystallographic analysis possible Resolution down to 0.2µm	Small depth of field
Scanning electron microscopy	Large depth of field Resolution down to 0.01µm Chemical analysis possible	Equipment expensive Colour information lost
Transmission electron microscopy	Resolution down to 0.001µm High-resolution chemical analysis possible Crystallographic (microstructural) analysis possible	Equipment very expensive Colour information lost Sample preparation difficult Image interpretation very difficult

Table1: Comparison of microscopical techniques

I.2 Chemical analysis in conjunction with electron microscopy

A side-effect of imaging using electrons (either by SEM or TEM) is that X-rays are produced which are characteristic of the chemical elements present. Analysis of the energies or wavelengths of these X-rays allows quantitative analysis of the elements present in the area illuminated by the electrons. There are a number of limitations to the technique as applied to real samples in the SEM. Particularly pertinent to samples of wood is the fact that unless surfaces are completely smooth, the analysis cannot be fully quantitative. Another limitation is that X-rays are generated not only in the area which the beam appears to illuminate, but also from surrounding regions (typically up to a micron in size). This means that analysis of a small region or a single particle is always subject to some doubt. TEM analysis does not suffer either of these limitations, and is generally capable of higher accuracy.

II Examples involving microscopical and chemical analysis of violins

II.1 Wood selection

When instrument makers select their materials, the choice is dictated by a number of factors. For many makers, the type of wood is determined by convention: traditionally, the tops of violins are made from Norway Spruce; the ribs and back from maple. But what is the rationale behind this? The criteria for back and front are different. The back is mainly concerned with providing mechanical support for the strings, and doing so with minimum mass. Its vibration properties are certainly important as well, but for many makers the precise choice of wood is determined more by appearance than by anything else.

The top has an important function as a soundboard, and to achieve greatest loudness this involves maximising the vibration amplitude of the plate. The strength must still be adequate for maintaining structural stability, but elastic modulus and acoustic damping of the wood are now of prime importance in determining the performance of different types of wood. The analysis [Barlow 1997] involves setting an appropriate minimum strength for the violin top, and then (using the vibration response of the arched plate) maximising the vibration amplitude. The wood which is optimised by this criterion is balsa, but this is ruled out by the strength criterion. Taking both criteria into account, the choice of spruce is optimal.

An instrument maker choosing wood may be influenced by its appearance: straightness and coarseness of grain are obvious attributes. To what extent does the appearance of the wood indicate its mechanical properties, and its suitability for instrument making? Even within the same wood species, there may be a considerable spread of mechanical properties (elastic modulus and strength in particular) and density. The properties are determined by the cell structure of the wood, and Fig. 1 shows the structures in a typical sample of Norway Spruce as viewed in the SEM. The tracheid cells which make up most of the material are seen running diagonally across the picture from bottom left to top right; the wall thickness varies dramatically between the late wood and the early wood. Elastic modulus and strength for this direction are found to vary approximately linearly with wood density. The anisotropy of the cells structure means that properties of wood vary very strongly with direction; the behaviour can be modelled [Ashby and Gibson 1988]. The ray cells make up a relatively small volume of the wood, but since they run normal to the strong direction of the tracheids the have a noticeable influence of the mechanical properties [e.g. Kahle and Woodhouse 1994].

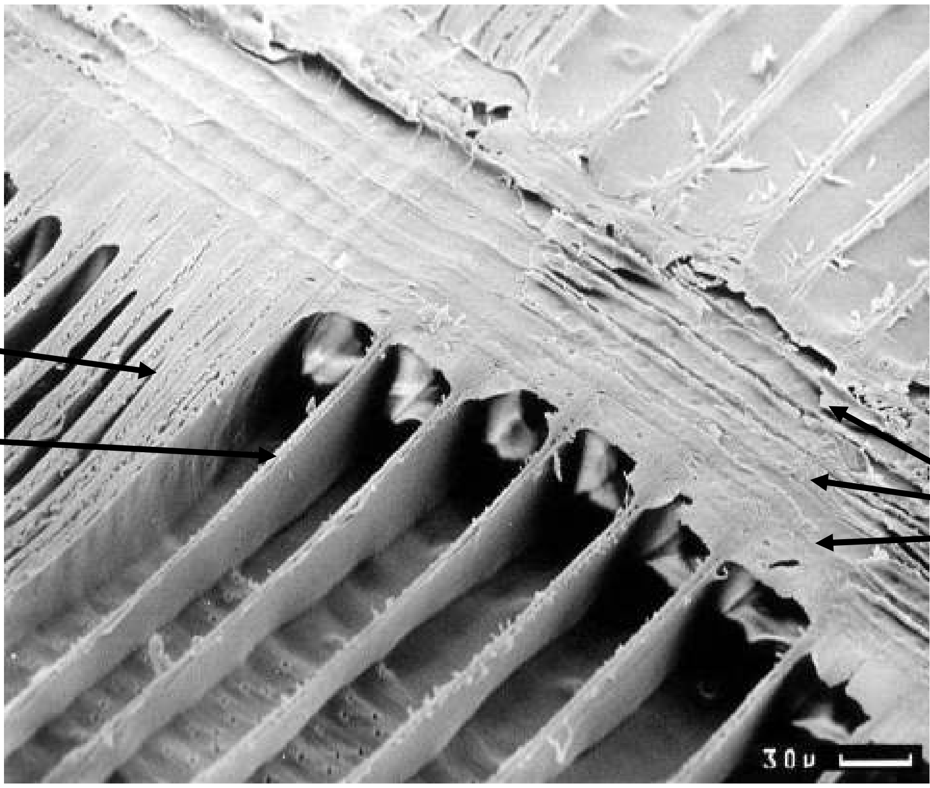

Figure 1. Cell structures in Norway Spruce, showing tracheids and ray cells.

II.2 Wood treatment

From time to time, theories are proposed that wood in old violins has been soaked or treated in some way, in water (salt or fresh) or in solutions of chemicals. One of the suggested chemical treatments is impregnation with borax: this is an obviously sensible proposal because of the well-known ability of borax to kill woodworm. Analytical methods for determining whether there is any evidence for such treatment involves chemical analysis of wood. This is a far from straightforward using techniques associated with electron microscopy because the principal element in borax, boron, has an atomic number of 5. The technique is rather insensitive to detection of elements at this end of the periodic table. In addition, wood contains a number of elements (including not only the "organic" constituents carbon, hydrogen, oxygen and nitrogen, but also appreciable quantities of the mineral-derived elements aluminium, calcium, iron, magnesium, manganese, sodium, phosphorus, potassium, silicon, sulphur and zinc), so detection requires measurement of changes in concentration rather than simply the addition of a new element. And as noted in Table 1, for any analysis of wood surface accuracy is compromised because wood surfaces are far from smooth.
A hypothesis which can be tested, however, is that wood had been soaked in water, or kept very wet. Brief periods of immersion were common, since transporting by floating was the easiest way to move timber around. Performed deliberately and for

periods of 4-12 weeks this is known as Ponding, and it renders the wood permeable to chemicals (e.g. for impregnation with preservative), and also more stable under demanding service conditions such as masts for ships [Rossell et al. 1973]. Under these conditions bacterial attack takes place, and the softest parts of the wood structures are destroyed. These include the membranes of the bordered pits in softwoods which act like valves linking tracheid cells. A dozen samples of spruce from old violins was examined to see if there was evidence of such attack [Barlow and Woodhouse 1990(a)]; in all cases (including a number of samples from Stradivari instruments) the central membrane discs (which are able to seal the valves) were intact. An example is shown in Fig 2 from an instrument by Maggini from 1610. Here, not only are the central membranes intact, but parts of the margo (the network of

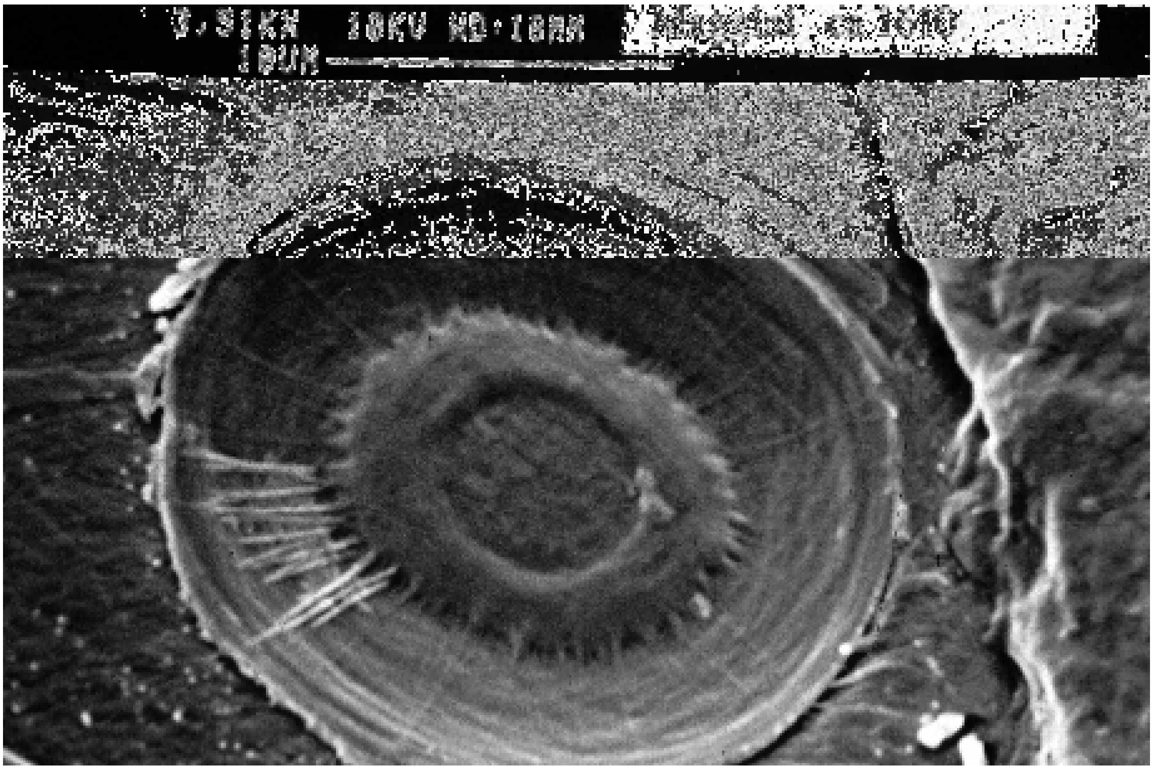

Figure 2. SEM picture of bordered pit in spruce from violin by Maggini.

which supports the membranes) can be seen. It is worth noting that despite the lack of evidence for ponding, very high concentrations of chlorine and sodium were found in a sample of wood from a violin by Santo Serafin, who was working from Venice. It would appear that some of his wood had been immersed in the sea. The immersion may have been done deliberately, although Serafin may not have desired wood in this state. Count Cozio di Salabue writing at that time commented: 'Good timber can usually be bought in Venice out of Istria. but be sure to get it before it has been carried to the Arsenal and been immersed in sea water to fortify it and stop the worm' [Dipper and Woodrow 1987].

II.3 Making techniques – bending

A recurrent debate is whether Golden Age violin plates were carved or bent. The arguments in favour of bending include noting that when plates are carved, the grain lines are cut so that strength may be impaired. Others note that plates in some old violins have very uniform thicknesses, and observe that this would arise naturally if flat plates were bent to shape.

In order to be bent to shape, wood needs to be 'plasticised' in some way so that it can be bent as required, and then will keep its new shape in a stable way once the stress is removed. This may involve heating with or without moisture. Examples are that violin ribs are commonly bent using only the heat from a bending iron (although it is normal to ensure that the wood is not too dry before bending is attempted); furniture is often bent using steam to plasticise the wood.

It is worth asking how the wood responds to bending, and whether it is damaged by the process. In order to investigate this, wood was plasticised using two different processes: steam, and ammonia. Unlike steam or water which have no lasting influence on the material, ammonia combines with the cellulose and permanently affects the mechanical properties of the wood. When impregnated with ammonia (which as a constituent of horse manure would have

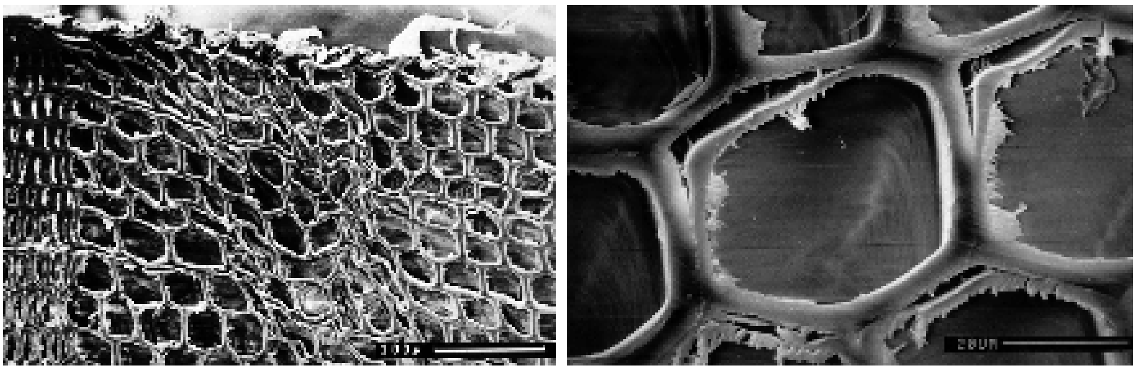

Figure 3. Spruce plasticised using ammonia, and then bent. (a) Macroscopic cell distortion, particularly in the early wood. (b) Failure of tracheids along the central lamella.

been readily available to early instrument makers) the wood is initially soft and pliable, and can be shaped without the use of heat. On drying, it becomes very hard, with increased elastic modulus [Barlow and Woodhouse 1992; Barlow and Woodhouse 1993]. With both ammonia and steam, however, there are signs that the wood is damaged by bending. The spruce in Fig.3 has been plasticised by ammonia and bent to shape; the cells in the earlywood are badly distorted. It can be seen in Fig 3b that the tracheids are pulling apart along their centre lines. This will have the effect of reducing the strength, and the elastic modulus (particularly in the transverse direction) will also be reduced.

II.4 Varnishing and surface finishing

There has been considerable discussion over the years of the possible influence of varnish on the sound and playing qualities of violins. A newly-finished violin played 'in the white' before varnishing is often reported as sounding different from the finished instrument. Making a proper assessment of whether this is so is difficult to achieve: performing good listening tests on violins is notoriously tricky. As a simpler experiment [Barlow and Woodhouse 1990(b)] samples of wood were prepared as for violin-making and varnished using different traditional materials, including spirit varnish and oil varnish. Even with this experiment interpretation of the results was not straightforward, but one clear conclusion was that varnish of any kind significantly increases the damping factor of the samples. The ear is very sensitive to detecting differences in damping on plate tap tones, and this observation is in agreement with the small but noticeable changes which have been reported in the literature [Schelleng 1968].

Since it appears that varnish does have an effect on the sound qualities of a violin, then it is very important to be able to control how far the varnish will penetrate into the wood. The depth of penetration may also influence the appearance of the instrument, particularly when coloured varnish is being used. On maple, for example, varnish penetrating the vessels will produce deeply coloured flecks which are not regarded as desirable. The vessels are clearly visible in the SEM image of a sample of maple (cut using a scalpel blade) shown in Fig. 4. The vessels are the oval shapes seen in the upper (lower magnification) part of the figure; in the lower picture, the tracheid cells (which make up the main part of the structure) and a ray are visible.

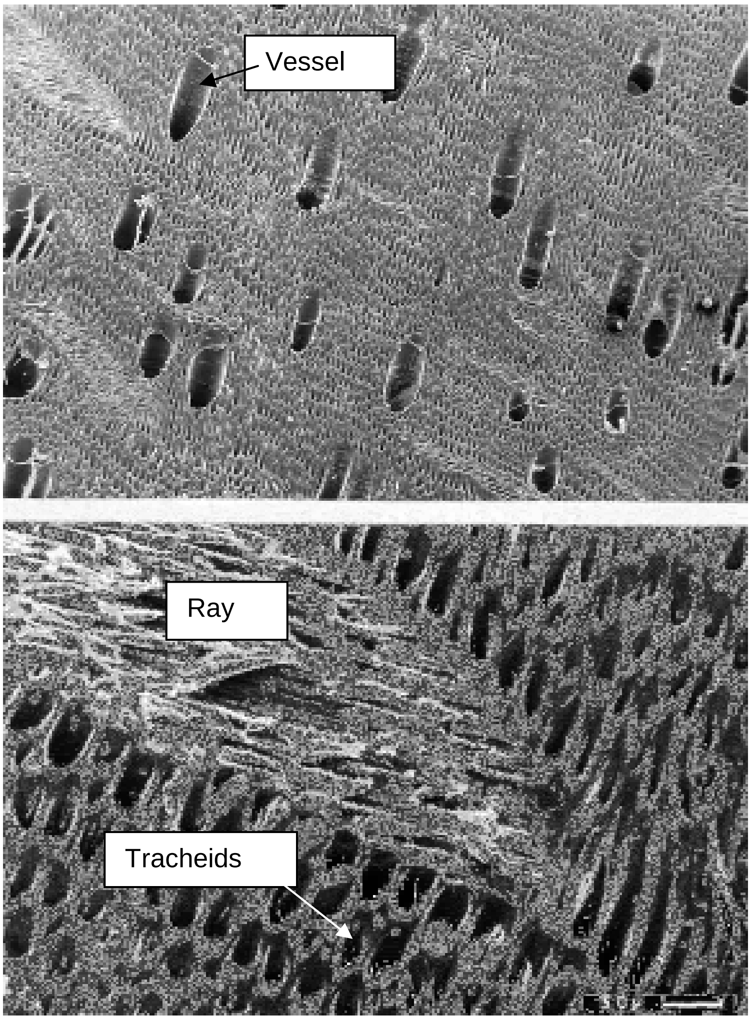

Figure 4. Cut surface of maple showing vessels, rays and tracheids.

In order to prevent varnish from penetrating wood, some sort of a barrier layer is required. The requirements for such a layer have been investigated, using experiments on contemporary samples together with examination of a number of samples taken from historic instruments. This was done as part of a more extensive investigation of the nature of ground layers in old violins [Barlow and Woodhouse 1987]. In some samples, mineral-rich « ground layers » were found between the wood and the varnish. One of the functions of these ground layers appeared to be that they acted as a barrier to the penetration of varnish.

Examples of this is shown in Fig. 5. In Fig 5a a « plug » is seen which prevents the varnish from penetrating a vessel in a violin by Nicolaus Amati (1660). This effect has been replicated in the experimental sample shown in Fig.5b, where a very thin layer of finely ground pozzolana ash has been used as a barrier layer. The pozzolana was applied in a water-based slurry, and allowed to dry. The wood surface was at this point completely obscured by the pozzolana powder. Rosin oil (a thin oil varnish) was brushed over the surface, which matched the

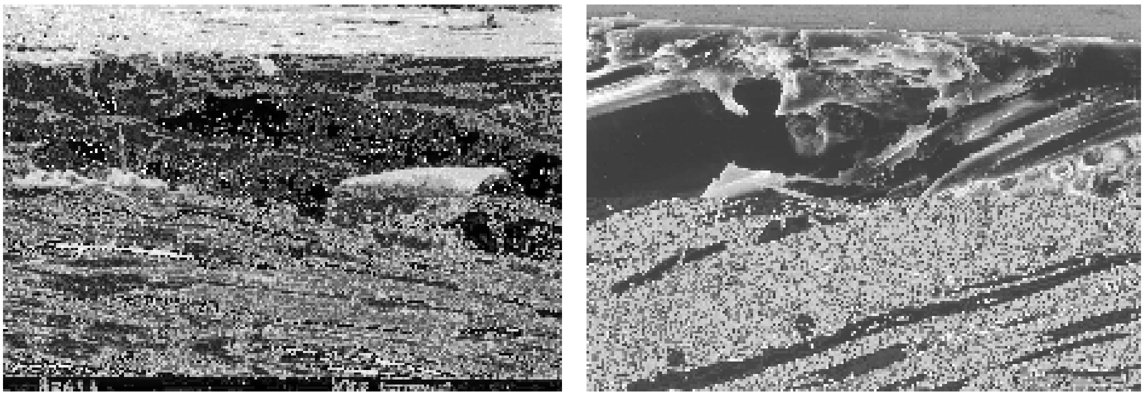

Figure 5a. Vessel in violin by Nicolaus Amati has been 'plugged' so that varnish cannot penetrate. The small spheres are fungal spores which were actively growing in the wood.
Figure 5b. Vessel in experimental sample which has been plugged by a thin layer of pozzolana ash in rosin oil.

refractive index of the pozzolana well enough that the layer became invisible to the naked eye. A thin varnish layer was brushed over the top of this. In Fig. 5b, it is not possible to discern the presence of the pozzolana layer. Similarly, in Fig. 5a there is no visible sign of a mineral barrier layer, but this study demonstrates that the absence of a visible mineral layer does not necessarily prove that one is not present. Much thicker layers have been found in other instruments (see Fig. 6), and although these often appear to have some function as barrier layers it is now evident that a barrier function might have been achieved using a very much thinner layer.
In the course of these investigations, the nature and function of mineral ground layers was investigated in a number of historic instruments. One of the questions to be answered was what the chemical composition was, and this was analysed alongside the SEM images. The results demonstrated that a wide range of materials was used, so that there was no single 'magic ingredient'. Even samples from Stradivari instruments of different dates showed very different chemical compositions, even though the appearance of the ground layers was very similar. The sample shown in Fig. 6 contained nearly 40% aluminium, 23% sulphur and 15% silicon. By contrast, another Stradivari sample contained between 10 and 20% of aluminium, silicon, sulphur, chlorine, calcium and iron.

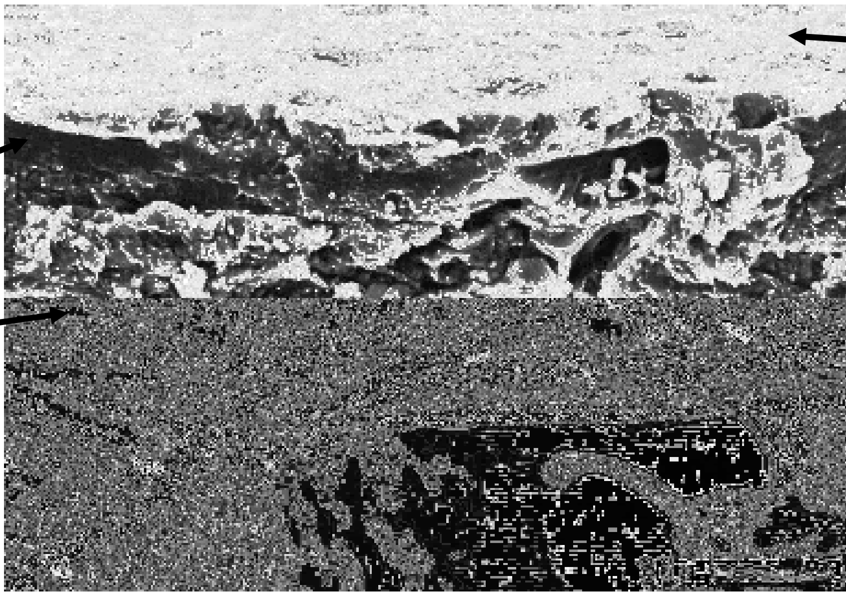

Figure 6. SEM picture showing section through a mineral ground layer on a Stradivari violin

III Conclusions

A number of examples have been used to illustrate the use of microscopical and chemical techniques for investigating and analysing wood and surfaces of violins. These studies have thrown some light on what was or was not done when violins were made in the 17th and 18th centuries in continental Europe. Some of the findings have proved useful to contemporary makers who are trying to replicate authentic techniques.

IV References

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Biography

Dr Claire Barlow is Senior Lecturer in the Engineering Department at Cambridge University, and specialises in the relationships between microstructure, mechanical property and processing in a wide range of materials. She has undertaken a number of « forensic studies » on old violins, looking at ground layers and aspects of wood treatment mainly using Scanning Electron Microscopy coupled with X-ray chemical analysis. The prime motivation has been to better understand what the Old Masters may have been aiming for in their craft, and to make this information accessible to contemporary makers.