Mobile NMR: An essential tool for protecting our cultural heritage

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ABSTRACT What is ‘cultural heritage’? Is it simply our legacy of physical artifacts – or is it our collective legacy as human societies – how we want to be remembered by future generations? With time, negligence, and even military conflict working to erase the past, we must ask: Can a better understanding of our shared heritage assist us in addressing cultural differences in the present day? And how can science both help us understand the historic record and work to preserve it? In this perspective article, we examine an emerging scientific method, mobile nuclear magnetic resonance (NMR), which can help us examine in a non-invasive way important objects and sites of our cultural heritage. Following these investigations, one can envisage ways for protecting our global heritage for future generations. For this purpose, we examine how this method can be used to non-destructively explore historical artifacts, which can lead to understanding the science behind the creation of these treasured items – paintings, frescoes, parchments, historical buildings, musical instruments, ancient mummies, and other artifacts. This perspective article follows few relevant examples from the scientific literature where mobile NMR has been applied in a non-invasive way to analyze objects of cultural heritage. One can envision possible future advancements of this technique and further applications where portable NMR can be used for conservation of cultural heritage. Copyright © 2016 John Wiley & Sons, Ltd.

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What is mobile NMR?

Mobile NMR, also known as portable NMR and unilateral NMR,[1] is a method that employs nuclear magnetic resonance at low fields by making use of permanent magnets and surface coils to transmit and collect the radiofrequency signal to and from a sensitive volume, which is external to the device. A challenge arising from the simple magnet design of these portable sensors is the inhomogeneous magnetic field; however, one can use these sensors to probe 1H relaxation and diffusion times at different depths in the sample, because these parameters are not affected by the magnetic field inhomogeneity.

There are two major advantages of these portable sensors, such as the Bruker Profiler®[2] and the Profile NMR-MOUSE®,[3] to studying precious objects of cultural heritage. First, the portable nature of these sensors allows for the measurements to be carried out on site, in the location where these objects are hosted, such as museums and archaeological sites. In certain cases, the object needs to be stored under defined temperature, humidity, and other special conditions, or in other cases, the object is too large to be studied by other methods. This is the case of a study performed on Ötzi, the Iceman,[4] a glacial mummy, which is now hosted in the cold room in the museum in Bolzano, Italy. It is not possible to study the mummy by MRI because of its large diameter due to the position of one of its arms; therefore, a portable instrument, one that can be brought to the mummy inside the preservation room at the museum, is ideal for studying such delicate samples. Archaeological sites are another example where the instrument portability is crucial; in these cases, the object of interest is part of a historical building and cannot be relocated; therefore, it needs to be investigated on site. Frescoes or painted walls in buildings represent a relevant example here, and the NMR-MOUSE was utilized to map the moisture content and the state of conservation of various frescoes, including the ones from the church of Nostra Signora del Sacro Cuore in Rome[5] and Villa Palagione in Volterra, Italy.[6]

The noninvasive nature of these sensors represents a second major advantage, and experiments such as relaxation, diffusion, and proton density measurements can be used to characterize objects of cultural heritage in a nondestructive way. This opens the path to studying objects as diverse as paintings, mummies, parchments, and musical instruments, objects that could not be previously investigated by other invasive techniques.

This perspective highlights some of the case studies where portable NMR sensors such as the Bruker Profiler® and the Profile NMR-MOUSE® have been applied to the field of cultural heritage, illustrating how NMR relaxation measurements can be used to assess the state of conservation of historical paper, distinguish between different paints used for the creation of a painting, examine the varnish and the wood density of master violins, and understand the bone degradation of ancient mummies and bones (Figure 1). A special feature of the NMR-MOUSE is its ability to perform measurements at different depths in the object, by collecting depth profiles, where proton densities can be determined at different depths in the sample with a depth resolution as low as 10 μm. This allows for the use of mobile NMR to monitor the state of...
precious objects of cultural heritage both at the surface and inside the objects, gaining a more comprehensive understanding of the overall state of conservation of the object.

**Mobile NMR applications**

**Historical paper**

Ever since the beginning, humankind felt the need to communicate, to express what we see, learn, and experience, as well as our thoughts, and share them with our peers and to preserve our cultural achievements for future generations. One way of preserving our history is in the written form, where we relate our historical facts, religious beliefs, and works of art through written word. Paper is one of the oldest types of material used to record historical and cultural data. Different degrees of damage to historical paper can be caused by several factors: the exposure of paper to chemical substances or to biological entities such as bacteria, fungi, or insects, storage conditions, and inadequate handling of the paper. Because the main ingredients of historical paper are cellulose and water, both of them rich in protons, this makes unilateral NMR the optimal method for the noninvasive assessment of the state of degradation of paper.

The first attempt at characterizing the degradation of historical paper nondestructively by NMR was reported by Blümich et al., where the authors used the NMR-MOUSE to investigate historical books dating from the 17th century. This study shows how the NMR-MOUSE can be used to distinguish different degrees of degradation (low, medium, and high) by analyzing the transverse magnetization relaxation times, which decrease both for cellulose and water with decreasing paper quality.

Relaxation measurements with unilateral NMR were further used to evaluate the aging of modern paper by oxidation reactions, corrosion effect caused by iron-gall ink on pages of the Codex Major, a musical anthology from the Collectio Altaempsiana (1600–1610) of Palazzo Altaemps in Rome, and to study the deterioration effects on the organization and properties of collagen and water in fragments from the Dead Sea Scrolls, a collection of ancient manuscripts from the late Second Temple period with great importance to the history of Judaism and Christianity.

Mobile NMR represents a nondestructive and very sensitive tool for studying the deterioration effects of historical parchments and books by full analysis of relaxation parameters, which relate to the state of water and collagen in the paper composition. Further analysis by unilateral NMR could help assess the state of conservation of historical paper stored under different conditions, and by understanding the effect the different storage conditions have on the state of the paper, one can recommend optimal conservation actions that must be taken in order to best preserve such important objects for future generations.

**Paintings**

From Renaissance to Contemporary art, many artists expressed their creativity in the form of paintings. Whether they represent a portrait or a landscape to more abstract figures, these paintings are extremely valuable artistic representations, and conservation science, in this case, implies methods for preservation of paintings; restoration, in the cases where the painting has been severely damaged; and even forensic science, to examine whether a painting is authentic or a fake.

Paintings have a complex multilayer structure, starting with a wooden panel or a canvas support, followed by preparation layers, the paint layers, and the varnish. Understanding the layer structure of a painting can lead to a better understanding of the techniques and materials used by the artist for creating the painting.
The feasibility of using the NMR-MOUSE for the investigation of paintings was first tested on model painting samples prepared following the recipes of old masters and consisting of a wood panel covered by a primer and a paint layer. Acquiring depth profiles through these models clearly shows the potential of using the NMR-MOUSE to distinguish the different layers of the paintings.\(^{[11]}\) The different layers are illustrated in the depth profiles by different amplitudes, indicating that each layer has different proton densities, which can be utilized for the noninvasive analysis of painting stratigraphies. This study also reports how the CPMG decays can be used to identify different types of paint used.\(^{[11]}\) The information extracted from the complex multilayer structure and the type of paint present in the painting can be used to understand the techniques involved in producing master paintings, proving that unilateral NMR is an ideal tool to noninvasively characterize the painting structure and the working practices of the artist.

Furthermore, Presciutti et al. applied this method on a series of Italian Renaissance master paintings in the Galleria Nazionale dell'Umbria in Perugia, Italy, proving that this technique is suitable for measuring the thickness of different layers, including canvas reinforcements, in historical paintings, with an accuracy about 20–30 μm.\(^{[11]}\)

The NMR-MOUSE proved to be a useful tool for the comparative analysis of materials and techniques used in paintings. Thus, when studying two paintings, The Dinner and The Dance, from the Pipenpoyse Wedding series made by the same artist with the same materials and methods, Fife et al. observed differences in the transverse relaxation times between the painted treated by a conservator (The Dinner) and the untreated painting (The Dance).\(^{[12]}\) This exemplifies the feasibility of this method to be applied for comparative analysis of paintings, opening the possibility of using this method to examine differences between authentic and forged paintings, where a comparative analysis could reveal differences in the techniques and materials used by the painter and by the forger.

Mobile NMR has proven to be a reliable tool for extracting information regarding the layer structure of paintings and the different paints used as well as information regarding the application of treatment to paintings. Furthermore, for the future, one can use this information to assess the authenticity of a painting, the presence of a hidden painting underneath a visible one, the most appropriate treatment to be applied to paintings, the most effective conservation conditions, and the materials needed for restoration of damaged paintings.

Several aspects of mobile NMR could still be improved, one of them being the depth resolution, where an increased resolution would enable a more clear differentiation of the layers composing the painting. At the moment, to acquire depth profiles with the NMR-MOUSE, the sensor has to be manually positioned at the surface of the point of interest in the painting. A future advancement of the sensor could include a more automated XYZ positioning system, which would be useful for acquiring 3D maps of the painting. A higher sensitivity coil could reduce the acquisition time, which would shorten the measurement time for these experiments facilitating the acquisition of the 3D maps.

### Historical buildings and frescoes

Some of the oldest wall paintings are found in the cave of El Castillo in Spain and are dated to be around 40,000 years old, which proves that since times as ancient as the Upper Paleolithic, people have tried to communicate through art and to use these paintings to preserve part of their culture for future generations.

The deterioration of wall paintings is affected by external conditions such as weather, pollution, temperature, humidity, and bacterial attack. The state of conservation can be analyzed by the NMR-MOUSE in terms of relaxation parameters, diffusion measurements, and depth profiling for proton density measurements. Of high interest is using the mobile NMR technique to assess the moisture content in buildings, where moisture can severely damage the art decoration on buildings such as wall paintings and mosaics and can damage at the same time the building material itself. Several studies in art conservation have used the NMR-MOUSE to map the moisture content within the building pores. Unilateral NMR was used to monitor the state of conservation of the frescoes in the Vasari house in Florence and to characterize the effect the chemical treatments, cleansing, and consolidation procedures have on these frescoes. Thus, Hahn echo and \(T_2\) measurements helped to identify the detachment of the painted film from the plaster and the influence of soluble salts on the pictorial film.\(^{[13]}\)

The same authors also recorded 2D maps of moisture content in the wall paintings in the Serra Chapel from ‘Chiesa di Nostra Signora del Sacro Cuore’ in Rome. These maps were represented in terms of Hahn echo amplitude, and they illustrate a shift to higher values of the distribution of effective relaxation times in places with outcropping salts.\(^{[3]}\)

Stratigraphy of historic walls and wall paintings was explored by mobile NMR at Villa Palagione and the Seminario Vescovile di Sant’ Andrea in Volterra, identifying different paint and mortar layers.\(^{[6]}\) The NMR-MOUSE was also used to analyze the Mosaic of Neptune and Amphitrite at Herculaneum, where depth profiles were used to unravel the stratigraphy of the decorated walls and undocuumented conservation treatment with wax. Different proton densities in the depth profiles recorded in the House of the Black Room indicate the difference in moisture content associated with different conservation treatments. The same study also reveals the different techniques for preparing the walls for painting in the Vila of the Papyri.\(^{[14]}\)

The portability of the unilateral NMR sensors is exceptionally useful for studying historical buildings and wall paintings and mosaics, where the sample could represent an entire archaeological site and cannot be relocated for measurements. Mobile NMR has been successfully applied to examine the stratigraphy of wall paintings and to monitor the moisture content within the pores of these painted walls. The presence of moisture in the building pores is a critical factor influencing the deterioration of the building and of the art decorating the building walls. Mapping the distribution of moisture in the wall paintings would provide valuable information for the restoration process. The NMR-MOUSE that is used for studying buildings and frescoes is a larger sensor with a larger penetration depth of 25 mm; this means that the field strength is lower for this magnet because the magnetic field decreases with distance from the magnet and the coil. The depth resolution of the larger sensors is also lower than that of the smaller sensors. Improvements in depth resolution and sensitivity of the 25 mm sensor could help in gaining a more detailed picture on the moisture content at different depths in the pores and speeding up the measurements, which could enable the recording of 3D moisture content maps in the walls.

### Musical instruments

Building a violin is an art that began with the Amati family in Italy around the year 1555, and since then, very few people could master this technique to create a truly memorable piece of art. Among
them history of art mentions the names of the Amati family, the Guarnieri family, and the Stradivari family.

Precious objects such as the violins are being scientifically investigated for three main reasons: revealing the elements involved in building a violin and how they correlate with the exquisite sound of a violin, to try to differentiate an authentic violin from a fake, and to find a way to preserve such remarkable artwork. Understanding the properties of the wood and the wood treatment can help gain an insight into all the aforementioned matters.

The NMR-MOUSE was applied for the analysis of both violins and bows with the aim of correlating the wood density and wood treatment to the age of the instrument. The advantage of the NMR-MOUSE is that it can be employed noninvasively for the investigation of violins and bows, being able to maintain the masterpieces of great artists intact during experiments.

A small selection of violins and bows of different ages and manufactured by different luthiers has been analyzed with the NMR-MOUSE in terms of depth profiles and transverse and longitudinal relaxation times. The profiles reveal two distinct layers—one corresponding to the wood and one to the varnish layer covering the wood. The analysis of proton densities from the depth profiles reveals an increase in wood density with increasing age of the master violin. In contrast to that, a decrease of the wood density with the fabrication year of the bows is observed. Moreover, when plotting relaxation times function of the average proton density obtained from depth profiles of the wood region, a clear separation between the wood used for building violins and the one used for the bows is observed. These results indicate that the age of the instrument could be correlated with the wood density; however, for the future, more data would need to be acquired on a larger number of instruments with the fabrication year ranging over a larger period of time. It would also be very important to analyze several instruments produced by the same luthier in order to be able to discriminate between changes in the NMR signal that occur owing to the different materials used by the different artists or owing to the aging of the instrument. These are important steps to be taken for future research of master instruments by mobile NMR in order to potentially use this method for the authentication of violins and in the selection of wood for producing master instruments. Improvements in the depth resolution of the NMR-MOUSE would be useful in identifying the presence of several layers of varnish on the wood, which could help better understand the techniques specific to each luthier for producing such valuable music instruments.

Ancient mummies and bones

Since ancient times, death was not considered the end but simply the passage to the afterlife. The ancient Egyptians considered that the preservation of the body after death, through mummmification, was very important for the passage and safe journey of the soul in the afterlife.

The Egyptians were not the only culture who would mummmify the deceased to prepare him or her for the afterlife. The first collection of mummmification is from the year 5000 BC, attributed to the Chincorco culture that was dated as far as 7000 BC on the Atacama Desert coast. The mummies found in Peru dating from the Inca period around 500 years ago are both artificial mummies of the dead kings and natural mummies of children sacrificed for the Inca religious beliefs. These were mummmified by the extreme coldness and dry mountain air, where they were taken for the sacrifice. Another natural mummy preserved by the very low temperatures is Ötzi the Iceman, a 5300-year-old glacier mummy found in the Alps on the border between Austria and Italy.

The NMR-MOUSE was used in a comprehensive study of ancient mummies and bones, including an Egyptian mummy head, a Peruvian mummy, and Ötzi, the Iceman, and a selection of modern and ancient bones. Including the bones of Charlemagne, the king of Franks and Emperor of the Holy Roman Empire between 768 and 814. Many of these ancient mummies and bones are very fragile and need to be kept under special conditions and very often cannot be moved from the museum where they are stored. The advantage of mobile NMR is that it is both mobile and noninvasive, and the measurements can be carried out on site without the need to relocate the mummy. The perfect example where the NMR-MOUSE was used to study a mummy under special conditions is the case of Ötzi, the iceman, who was analyzed by the NMR-MOUSE inside the cold room at the Ötzi museum in Bolzano, Italy, where it is preserved at a constant temperature of −6.12 °C and constant humidity of 99.42%.

The NMR-MOUSE proved to be able to differentiate single layers of mummy bandages versus underlying tissue on an isolated mummy hand and to discriminate different soft and hard tissue layers, both in dry and frozen mummmified tissue and bone. An additional layer was observed for Ötzi, and it was assigned to the ice layer covering Ötzi’s body, responsible for his conservation at −6.12 °C. Furthermore, NMR amplitude varies across the skull in concordance with the organic bone density, and deteriorated bone materials from an ancient mummy and historic skeletons show lower bone density. In an analysis of tibiae, when comparing the amplitude of the profiles recorded on an old tibia and the tibia of Charlemagne, a much higher signal intensity is observed in the case of Charlemagne’s tibia, which could be caused by organic substances used for the treatment of the bones to ensure good preservation of the remains of Charlemagne.

Mobile NMR could prove to be an asset in establishing strategies for conservation of ancient mummies and bones. Continuous monitoring of proton density in mummies and bones could become a method of assessing their conservation state over time, detecting which are the causes leading to the deterioration of the bones and establishing the ideal conservation conditions for these important assets of cultural heritage.

It is our duty to preserve our global heritage for future generations, to preserve both the art itself and the traditions behind the art, to work on understanding why and how those artifacts were made and what do they represent for that society and for the global heritage.

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