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Noninvasive Testing of Art and Cultural Heritage by Mobile NMR†

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CONSPECTUS

Nuclear magnetic resonance (NMR) has many applications in science, medicine, and technology. Conventional instrumentation is large and expensive, however, because superconducting magnets offer maximum sensitivity. Yet NMR devices can also be small and inexpensive if permanent magnets are used, and samples need not be placed within the magnet but can be examined externally in the stray magnetic field. Mobile stray-field NMR is a method of growing interest for nondestructive testing of a diverse range of materials and processes. A well-known stray-field sensor is the commercially available NMR-MOUSE, which is small and can readily be carried to an object to be studied.

In this Account, we describe mobile stray-field NMR, with particular attention to its use in analyzing objects of cultural heritage. The most common data recorded are relaxation measurements of ^{1}H because the proton is the most sensitive NMR nucleus, and relaxation can be measured despite the inhomogeneous magnetic field that typically accompanies a simple magnet design. Through NMR relaxation, the state of matter can be analyzed locally, and the signal amplitude gives the proton density. A variety of stray-field sensors have been designed. Small devices weighing less than a kilogram have a shallow penetration depth of just a few millimeters and a resolution of a few micrometers. Access to greater depths requires larger sensors that may weigh 30 kg or more.

The use of these sensors is illustrated by selected examples, including examinations of (i) the stratigraphy of master paintings, (ii) binder aging, (iii) the deterioration of paper, (iv) wood density in master violins, (v) the moisture content and moisture profiles in walls covered with paintings and mosaics, and (vi) the evolution of stone conservation treatments. The NMR data provide unique information to the conservator on the state of the object—including past conservation measures.

The use of mobile NMR remains relatively new, expanding from field testing of materials such as roads, bridge decks, soil, and the contents of drilled wells to these more recent studies of objects of cultural heritage. As a young field, noninvasive testing of artworks with stray-field NMR thus offers many opportunities for research innovation and further development.

1. Introduction

Nuclear magnetic resonance (NMR) is the physical resonance phenomenon of magnetic atomic nuclei that precess in a magnetic field.[1,2] It has found important and widespread use in multiple areas of science and technology. These include Chemistry for molecular analysis,[2] Medicine for diagnostic imaging,[3] Geophysics for logging oil wells,[4] Materials Science, Biology and many others. The technique involves the magnetization of a sample or object of interest in a magnetic field, where the nuclear magnetization precesses

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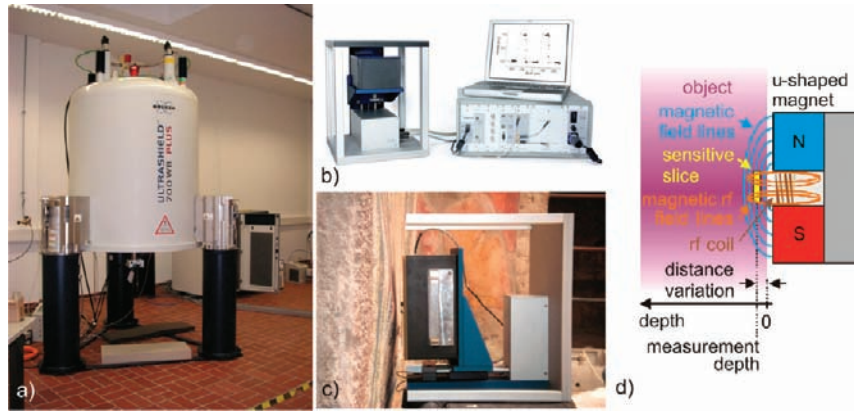

FIGURE 1. Magnets for NMR. (a) Superconducting high-field NMR magnet for high-resolution NMR spectroscopy in the laboratory. The sample is centered inside the magnet. (b) NMR-MOUSE (black) mounted on a computer-operated lift (blue plate), compact spectrometer, and computer for measurement. The object to be measured is placed on the black plate above the NMR-MOUSE. (c) Large version of the NMR-MOUSE mounted on a support for lateral displacement to measure profiles up to 25 mm depth into a wall. (d) Principle components of the NMR-MOUSE and measurement arrangement.

around the magnetic field following excitation with a radio frequency (RF) impulse. There is common agreement, that this field should be strong for highest sensitivity, as then both the nuclear polarization and the precession frequency are high, and the field should be highly homogeneous to resolve the small differences in precession frequency which are needed for chemical analysis. This is why modern NMR magnets produce field strengths of several Tesla with a homogeneity of better than 0.1 ppm across the sample dimensions. These magnets are bulky and need to be maintained at low temperature by cooling superconducting coils with liquid nitrogen and liquid helium (Figure 1a). NMR measurements, therefore, are typically executed in special laboratories, and the materials to be investigated are brought to the laboratory to be positioned inside the magnet where the field is most homogeneous.

This type of NMR is ill suited for analysis of objects of cultural heritage which often are larger than the opening of the magnet and cannot be moved from their location. Only with the availability of portable, one-sided instruments[5,6] did NMR qualify for testing objects that have to remain at their site and often may not even be touched. The use of NMR for nondestructive testing in the field of cultural heritage is still limited as the benefits of NMR investigations are often unknown and operation of the instrument requires a considerable user training. To address these points, a short introduction to NMR is given below followed by a report of representative results of NMR investigations on paintings, paper, violins, building, and conservation materials.

2. Mobile Single-Sided NMR

2.1. Stray-Field NMR. Well-logging NMR devices work differently from NMR machines for chemical analysis and medical imaging. For logging a well, a permanent magnet and the associated electronics are compacted into a temperature- and pressure-resistant pipe that is lowered into the bore hole of a well for inspection of the walls in the search for oil. Two aspects are different: the NMR device is moved to the site of measurement, and the magnet is positioned inside the sample and not the other way around. Although this technology was envisioned 60 years ago, it took nearly 50 years to overcome the technological challenges so that NMR well-logging was commercialized only in the mid 1990s. Early on it was recognized, that related, small and mobile NMR instruments would be useful for inspection of various goods and technical processes.[5] A variety of NMR sensors was built for different applications, and ideas were generated on how to improve the magnet to generate a remote region of strong and homogeneous magnetic field in accordance with the laboratory-NMR philosophy. The advantages of such NMR devices are that large objects such as roads, bridge decks, and soil can be investigated locally and noninvasively at their original location for moisture content and other properties.[6] This type of NMR machine is also suitable for analyzing objects of cultural heritage.

2.2. NMR-MOUSE. Eventually it was realized, that NMR signal can be obtained also in highly inhomogeneous stray fields of magnets[7] by observing NMR echoes such as Hahn echoes[8] and trains of such echoes as worked out by Carr, Pur-

cell, Meiboom, and Gill (CPMG) in the early days of NMR.[9,10] While the first stray-field experiments were carried out with superconducting magnets, simple permanent magnets small enough to carry along can also be used as well.[6,7] This fact and the insight, that magnetic resonance imaging (MRI) employs magnetic fields with time-dependent inhomogeneities to generate images rich in contrast for soft matter analysis led to the development of the NMR-MOUSE (mobile universal surface explorer)[11] at about the same time well-logging NMR was commercialized. The NMR MOUSE is a palm-size NMR device with a time-invariant stray field that is positioned near an object to measure the information of one pixel of a medical image from a volume fraction of the object near the sensor (Figure 1b). Contrary to MRI, the NMR-MOUSE is ideally suited for nondestructive testing of large objects at the site of the object, although large depths cannot be accessed.

The NMR-MOUSE is the first small stray-field NMR sensor that could be conveniently transported. In its original design, it consists of a u-shaped magnet with a RF coil in the gap between the poles. This arrangement of magnet and coil produces a sensitive volume external to the device, from where the signal is collected. But this volume is oddly shaped for simple magnets. It is curved and varies in thickness. A major breakthrough was to modify the magnet arrangement in such a way, that the sensitive volume becomes a thin, flat slice parallel to the sensor surface.[12] With this Profile NMR-MOUSE depth profiles can be acquired with high resolution by shifting the sensitive slice in steps through the object along the depth direction (Figure 1d). A record depth resolution of 2.3 μm could be achieved. This device appears to be the most useful tool for analysis of objects of cultural heritage. It can be employed wherever hydrogen is present, as the proton NMR signal is detected, and whenever the objects are not electrically conducting and free of magnetic parts. If nails or other iron parts are nearby, special care has to be exercised to account for the attractive forces between the magnet of the NMR sensor and the magnetic object.

Today the technology of NMR with small and mobile magnets is rapidly evolving due to advances in shaping the magnetic field emanating from permanent-magnet arrays.[6] While the stray-field of the Profile NMR-MOUSE is optimized for a constant magnetic field gradient over an extended plane, the stray field can also be shimmed to extreme homogeneity sufficient to measure chemical shifts in a solution-containing flask on top of the magnet.[13] The underlying idea of shimming is currently being applied to the development of coffee-cup size magnets[14−16] that accommodate conventional 5 mm diameter NMR sample tubes for chemical-shift resolved spectroscopy, which, along with single-chip NMR spectrometers,[14] are believed to eventually lead to cell-phone size NMR spectrometers for chemical analysis of small molecules.

2.3. Mobile NMR for Analysis of Objects of Cultural Heritage. The idea to use the NMR-MOUSE for inspection of objects of cultural heritage was promoted by the late Annalaura Segre, to whose memory this Account is dedicated. The Profile NMR-MOUSE is available today in different sizes corresponding to different depth ranges.[17] The larger the depth range, the larger the sensor. Standard depth ranges are 3, 10 (Figure 1b), and 25 mm (Figure 1c). As the magnetic field falls off with distance from the magnet and the coil, the field strength is lower for sensors with a high depth range and so is the amplitude of the received signal. To compensate for the signal loss, the volume of the sensitive slice is made larger for sensors with high depth ranges. As it is difficult to align a laterally extended sensitive slice with the layer structure of an object, the depth resolution of sensors with a high depth range tends to be lower than that of sensors with a short depth range. Paint layers, paper, and conservation treatments are best analyzed with a 3 mm sensor, wood and bones with a 10 mm sensor, and moisture in building materials with a 25 mm sensor.

For operation, the NMR-MOUSE is mounted on a computer-controlled precision lift, which is positioned close to the object, so that the sensitive slice is at the desired depth or at the maximum depth inside the object (Figure 1c,d). Measurements are then conducted by acquiring a NMR signal at each depth and retracting the sensor from the object step by step. This procedure avoids forward motion of the sensor that may damage the object.

The signal acquired at each depth can be generated by a multitude of NMR schemes that work in inhomogeneous magnetic fields.[6] Often the signal amplitude, the NMR relaxation times T_1 and T_2, the self-diffusion coefficient D as well distributions of T_1, T_2, and D are measured by echo techniques. The signal amplitude is proportional to the number of protons in the sensitive volume and a good indicator for moisture content. The relaxation times and the diffusion coefficient scale with the molecular mobility in materials such as segmental motion in polymers and translational motion of small molecules in liquids embedded in the pores of wood and stones. Slow motion correlates with short and fast motion with high T_2 and D. Distributions of these parameters are obtained by inverse Laplace transformation of NMR signals acquired with suitable sequences of RF impulses.[18,19]

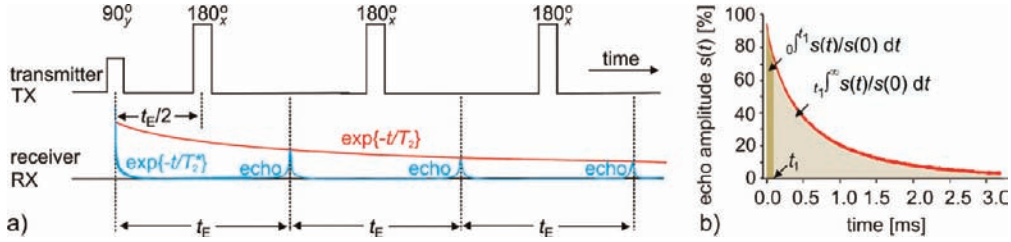

FIGURE 2. (a) NMR excitation and response. The NMR response to an RF impulse is voltage induced in the RF coil by the nuclear magnetization precessing about the direction of the applied magnetic field B_0 with frequency $\omega_0 = \gamma B_0$, which decays with time constant T_2. In inhomogeneous fields, different frequencies are observed in different volume elements of the object, and the impulse response decays rapidly with time constant T_2^* by destructive interference of the signal contributions. Echoes can be generated with 180° impulses, the peaks of which stroboscopically sample the homogeneous-field decay. (b) Envelope of a CPMG train of echoes and definition of partial integrals for calculation of the contrast parameter w.

2.4. Measurement and Analysis. The NMR technique used most with the NMR-MOUSE is the CPMG sequence (Figure 2a).[20] With it a train of NMR echoes is acquired in the inhomogeneous stray field of the sensor. Because of the field inhomogeneity, the impulse response decays rapidly as the NMR signals from different volume elements interfere destructively. This destructive interference is removed in the NMR echo. A train of echoes then stroboscopically samples the signal decay of the transverse magnetization in a homogeneous magnetic field, and the amplitude and shape of the echo-train envelope are the prime source of information in stray-field NMR. As an aside it is noted that, in strongly inhomogeneous magnetic fields, where each RF impulse excites a limited part of the sample volume, the echo-train envelope only approximates the decay of the impulse response in homogeneous field, because resonance offset effects cannot be suppressed. This is why the T_2 relaxation times retrieved by stray-field NMR are referred to as $T_{2\text{eff}}$.[6]

The acquired echo-train envelope $s(t)$ can be processed in different ways.[6] The most general approach is to compute the distribution of relaxation times by inverse Laplace transformation, following the assumption, that $s(t)$ can be written as a sum of many exponential functions with relaxation times $T_{2\text{eff},i}$

$$s(t)/s(0) = \sum_i x_i \exp\{-t/T_{2\text{eff},i}\} \quad (1)$$

where x_i is the relative weight or mole fraction of the component with relaxation time $T_{2\text{eff},i}$ in the sensitive volume. For many materials-analysis applications, however, knowledge of all x_i and $T_{2\text{eff},i}$, that is, of the relaxation time distribution, is more information than needed when a comparative characterization of an unknown property relative to a known property suffices. This scenario is typical for NMR imaging, where image contrast identifies variations of parameters between pixels that reveal the heterogeneity and thus different material properties of the object under study. In fact, different contrast parameters can be derived from $s(t)$.

The relative spin density of fraction i is given by x_i. The value of $x_i \exp\{-t/T_{2\text{eff},i}\}$ at a particular $t = t_1$ introduces a T_2 relaxation weight to the spin density. A T_1 weight is introduced when repeating the measurements with a short recycle delay. T_1 is the time constant for build-up of thermodynamic equilibrium magnetization. In heterogeneous objects, individual fractions i may differ in their values of T_{1i}. If the recycle delay $t_R < 5T_{1i}$, then the magnetization component i cannot fully recover and only those magnetization components j are detected at full amplitude for which $t_R > 5T_{1j}$.

A contrast parameter w, which is often used in the measurement of depth profiles with the NMR-MOUSE is defined as the ratio of the integrals of the initial part of $s(t)$ and the remaining part of $s(t)$ (Figure 2b)[6]

$$w = \left({}_{t_1}\int^{\infty} s(t)\mathrm{d}t\right) / \left({}_{0}\int^{t_1} s(t)\mathrm{d}t\right) \quad (2)$$

The dimensionless number w can be approximated for $t_1 \ll 5\,T_{2\text{eff,shortest}}$ by

$$w \approx \left({}_{0}\int^{\infty} s(t)/s(0)\mathrm{d}t\right) / \left({}_{0}\int^{t_1} s(t)/s(0)\mathrm{d}t \propto \langle T_{2\text{eff}} \rangle\right) \quad (3)$$

where $\langle T_{2\text{eff}} \rangle$ is a number-averaged transverse relaxation time

$$\langle T_{2\text{eff}} \rangle = \sum_i x_i T_{2\text{eff},i} \quad (4)$$

Depending on the choice of t_1 in eq 2, the contrast can be adjusted without resorting to parametrization of the measured signal via a fit with a model function.

Another source of contrast in objects permeated by fluids is the echo time t_E, that is, the time lag between successive echoes of the center-to-center separation of the 180° impulses in the CPMG sequence (Figure 2a). Because of the strong gradient of the NMR-MOUSE, the decay of the echo-train envelope is enhanced by translational diffusion of the magnetization-carrying molecules when moving from one value of the magnetic field to another in between impulses. By increasing the echo time, contrast by diffusion is enhanced.

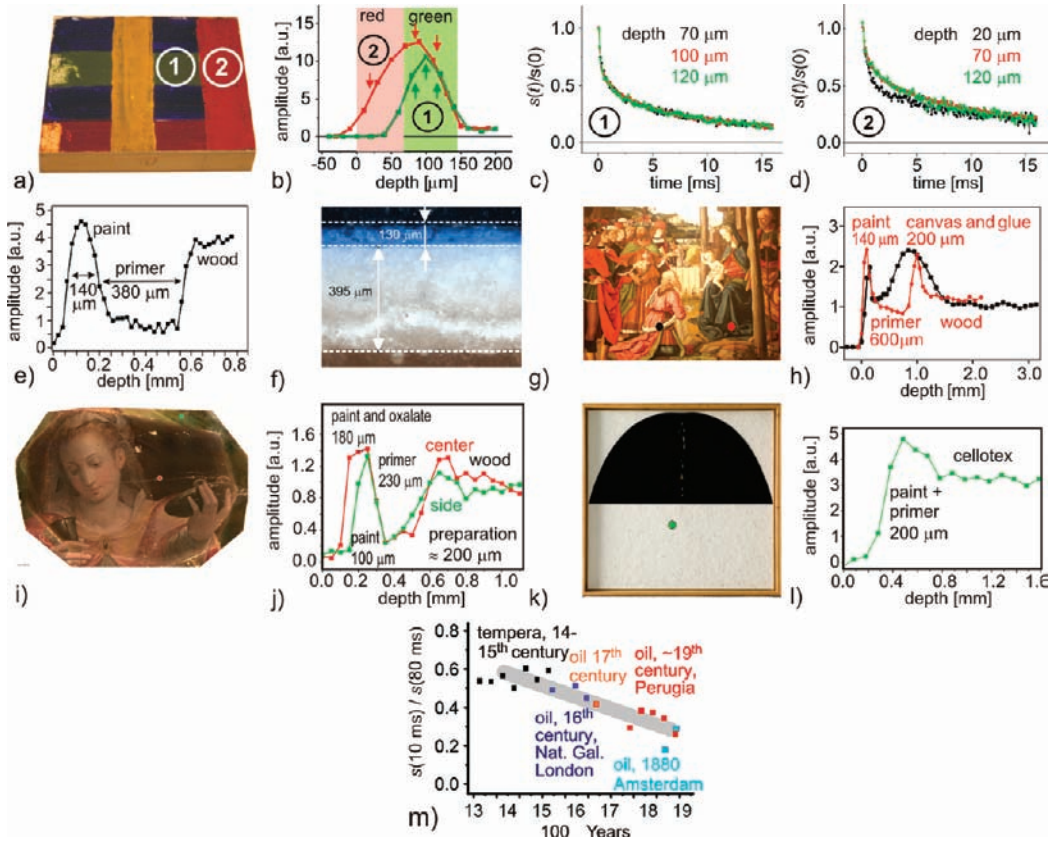

FIGURE 3. Depth profiling of paintings. (a) Easel painting model consisting of wood covered with a primer and one (1) or two (2) paint layers. (b) The depth profile (1) for one paint layer is thinner than that (2) for two paint layers. (c) Echo-envelope decays at different depths for one paint layer. (d) Echo-envelope decays at different depths for two paint layers. The paint layer from position (1) shows up at 120 μm depth. (e) NMR depth profile through a painting model which identifies the layer thicknesses of paint and primer. (f) Depth profile through the same painting model measured invasively by optical microscopy. (g) Photo of "Adoration of the Magi"(1470) by Perugino and positions of the measured depth profiles. (h) Depth profiles at the two marked positions revealing differences in the thickness of the textile layer. (i) Photo of a detail of "Pala Albergotti" (1570) by Giorgio Vasari and locations of the measured profiles. (j) Depth profiles at the indicated positions. They show different thicknesses of the painting layers in the center of the painting and under the frame. (k) "Bianco e nero" (1971) by Alberto Burri. The point marks the location of the measured depth profile. (l) Because PVA was used as a binder for both, the paint and the primer, both layers give rise to one signal in the depth profile. (m) Longitudinal relaxation weights of paint layers with oil and tempera binders from several centuries. NMR can detect aging of paint layers over five centuries.

3. Applications

The use of mobile stray-field NMR sensors[6] receives ever increasing attention by art historians and art conservators. In the field of cultural heritage, they have been applied to study stone conservation and to analyze wall paintings, wood and paper, old master paintings, and mummies.[6]

3.1. Paintings. The suitability and accuracy of mobile stray-field NMR with the NMR-MOUSE were tested on easel painting models (Figure 3a), which had been prepared following the recipes of the old masters.[21] They consisted of a wood panel covered by a primer composed of gypsum and animal glue and a paint layer containing pigments mixed with egg tempera. Composite paint layers could be identified by the thickness of the layers (Figure 3b), and the type of paint could be identified by differences in the CPMG decays at different depths (Figures 3c,d). To demonstrate the performance of the NMR sensor, depth profiles were measured noninvasively by NMR (Figure 3e) and compared to cross sections from optical microscopy of samples extracted from the panels (Figure 3f). The layer-thickness values determined optically and by NMR agree within an accuracy of 10−15 μm.

The technology was subsequently applied to unravel the stratigraphy of old master paintings (Figures 3g,h).[21] In the painting "Adoration of the Magi" (Figure 3g) by Perugino, differences in the thickness of the textile layer covering the wood underneath the primer were found at two positions (Figure 3g). The layer is thicker, where two wooden boards are joined. A difference in the paint-layer thickness was identified in the painting "Pala Albergotti" by Giorgio Vasari in the center and on the side under the frame (Figures 3i,j). From a combined

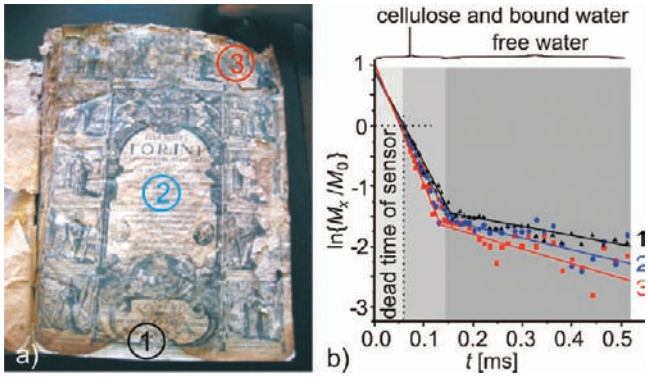

FIGURE 4. Book from 1605 showing evidence of biological attack due to water damage. (a) NMR measurements were conducted at the three positions marked. (b) In the logarithmic presentation of the experimental NMR data, the signals of bound and free water in the cellulose matrix can be identified. The signal from the cellulose matrix relaxes within the dead time of the sensor. The damage progresses from position 1 to position 3. Lines are drawn to guide the eye.

analysis by optical microscopy and FT-IR spectrometry this difference is ascribed a thick layer of oxalates, which derives from the degradation of a protein finishing layer.[22]

Contemporary art employs a wide variety of materials of different vulnerability and complexity that challenge the NMR analysis. In his painting "Bianco e Nero" (Figure 3k), the famous Italian contemporary artist Alberto Burri uses synthetic poly(vinly acetate) (PVA) as binder instead of conventional oil or tempera.[23,24] The NMR depth profile through the painting reveals that the same binder was used for both, the paint and the primer (Figure 3l).

The aging of conventional binders is associated primarily with changes in T_1 and less with changes in T_2.[21] It has been followed in terms of a longitudinal relaxation weight by analysis of a considerable number of master paintings that date back over more than five centuries (Figure 3m). T_1 shortens with increasing age indicating a trend toward a more a brittle texture of older binder.

3.2. Paper. Old paper is made mainly from pure cellulose, and the main components of wood are cellulose and lignin. Both materials contain bound and free water. The organic host material and the water can give rise to ^{1}H NMR signal. In damaged paper and wood, the amounts of water, the molecular weight, and the crystallinity of the cellulose molecules have changed. These changes can be followed by measuring relaxation times (Figure 4).[25] Progressive paper damage leads to decreasing relaxation times of bound and free water. In an artificial aging study of paper, the results obtained by single-sided NMR have been shown to be in good agreement with those obtained by NMR in homogeneous fields.[6] Corrosive effects of iron gall ink on paper were detected in the Codex Major of the Collectio Altaemsiana. Different inks have different effects on the NMR relaxation times. Even faded inks can in some cases be detected. Moisture and degradation in wooden objects have also been studied by single-sided NMR.[6]

3.3. Violins and Bows. Stradivari is the most famous violin maker of all times. To unravel the secret of his violins is a topic of continuing interest.[26,27] Part of the exquisite sound of good master violins is attributed to the selection of the wood and another to the wood treatment. A small selection of master violins has been analyzed with the NMR-MOUSE in terms of depth profiles (Figure 5a).[28] These reveal the varnish layer and provide a signal from the wood (Figure 5b). In some cases there were indications of two or more varnish layers, and considerable differences were found in the signal amplitudes of the wood. The signal shown in the depth profiles derives mostly from the material density and only marginally from the softness of the material. When plotting the signal amplitude at 0.7 mm depth over the reported fabrication year of the violins, an increase of the wood density with the age of the violin was found for most master violins investigated (Figure 5c). In contrast to that, the wood density of the precious bows investigated decreased with age. This is strong evidence, that the wood density is an indication for the age of the instrument and that it plays a vital role in the quality of master violins and bows. This information can be used in the selection of wood for producing modern master instruments and as evidence in the authentication of master violins. Outliers may identify suspicious instruments that need further investigation.

3.4. Buildings. The time-dependent water uptake and drying of stone can be followed by the evolution of various NMR parameters such as relaxation times, the signal amplitude, and the relaxation time distribution. The NMR-MOUSE is well suited to quantify moisture content in terms of the proton signal amplitude, but the apparent relaxation times are affected by translational diffusion and do not as readily correlate with the pore size of fully saturated porous media as relaxation times do that have been determined in homogeneous field.[6]

Most walls in buildings are naturally moist. As the moisture breathing of walls determines the fate of wall decorations, moisture maps give important information to restorers on the state of wall paintings and mosaics. The frescoes in Vasari's house in Florence from the 16th century have been analyzed for moisture by NMR,[29] as have frescoes by Pellegrino degli Aretusi in the Cappella Serra of the church of Nostra Signora del Sacro Cuore in Rome (Figure 6a–c).[6] The latter (Figure 6a) were painted between 1517 and 1519 and suffer from moisture rising from underground. The moisture was mapped in terms of the Hahn echo amplitude (Figure 6b).[30] A

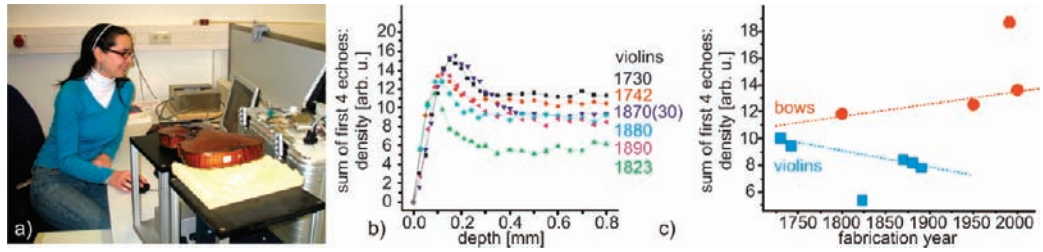

FIGURE 5. (a) Set-up used in a study of master violins by the Profile NMR-MOUSE. The violin back rests on top of the lift depicted in Figure 1b. Photographed by B. Blümich with permission by Maria Baias. (b) NMR depth profiles according to proton density through the back of different master violins. (c) Wood density of backs of violins at 0.7 mm depth for different claimed master violins and bows versus the reported fabrication year.

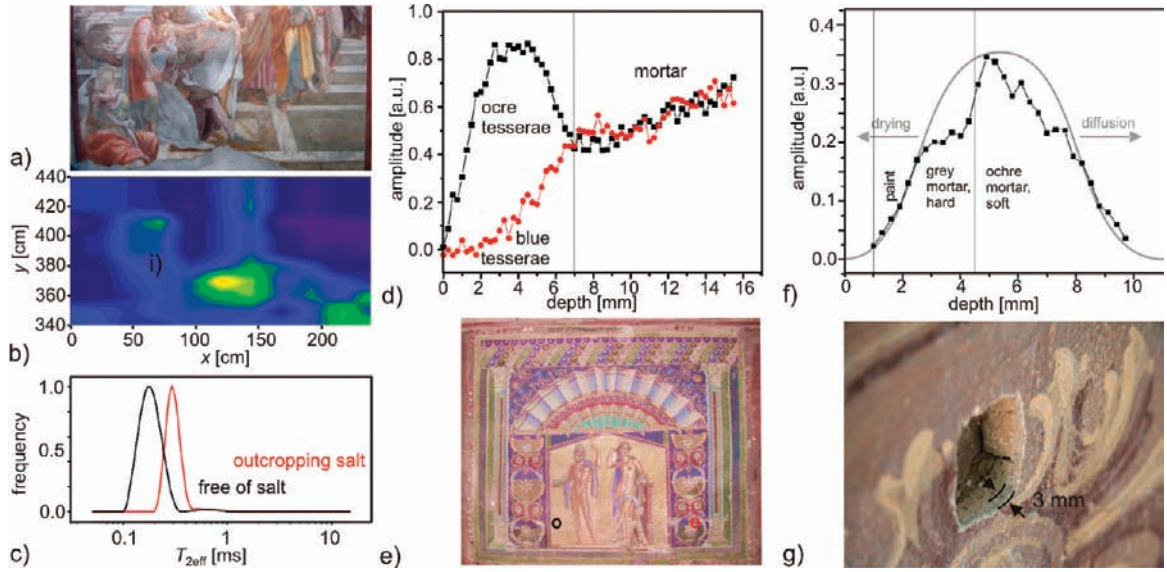

FIGURE 6. Analysis of walls by NMR depth profiles. (a) Fresco by Pellegrino degli Aretusi in the Capella Serra of the Church of Nostra Signora del Sacro Cuore in Rome (painted between 1517 and 1519). (b) Contour plot of the Hahn-echo amplitude which maps the moisture content. Dark denotes dry and light denotes wet. (c) Outcropping salts invoke a shift of the distribution of effective relaxation times toward higher values. (d) Profiles of natural moisture at two positions of the mosaic from Neptunus and Amphitrite in Herculaneum measured with the setup of Figure 1c. The blue tesserae are dry; the ochre ones are wet. The mortar bed at both positions shows the same moisture profile. (e) Photo of the mosaic with measurement positions marked. (f) Depth profile through a painted wall inside Villa Palagione in Volterra measured in 10 h after spraying the wall with water. It reveals a step at 3 mm depth. This corresponds to a change in mortar consistency. (g) Photo of the mortar layers after opening up the wall at the measurement position. The outer layer of more dense mortar is 3 mm thick.

shift of the T_{2eff} distribution was observed in places with outcropping salts (Figure 6c), and the values of the transverse relaxation time were found to correlate with past cleansing and restoration efforts.

A Profile NMR-MOUSE with 25 mm depth access has been employed to investigate the moisture content of the world cultural heritage mosaic of Netpune and Amphitrite in Herculaneum (Figure 6e).[31] Moisture is a key concern in the conservation efforts of the excavation site. Depth profiles measured at two positions through the mosaic reveal a large difference in moisture uptake of two different types of tesserae and the same moisture profiles for the mortar embedding the mosaic stones (Figure 6d). The results of such measurements are expected on the one hand to help identify suitable conservation strategies and on the other hand to detect undocumented restoration efforts of the past.

High moisture content provides good NMR signal and short acquisition times like 20 min for one of the depth profiles of Figure 6d. The natural moisture content of dry walls is much lower, and the acquisition time for one depth profile may extend to several hours. This may be somewhat shortened when spraying the wall to be measured with water prior to examination. This has been done in an investigation of the painted walls in the state room of Villa Palagione, Volterra, Italy, which was built in 1598.[32] During the measurement time of about 10 h, the moisture applied to the surface migrated into the interior of the wall and dried from the outside. Nevertheless, at 3 mm depth, a step was observed indi-

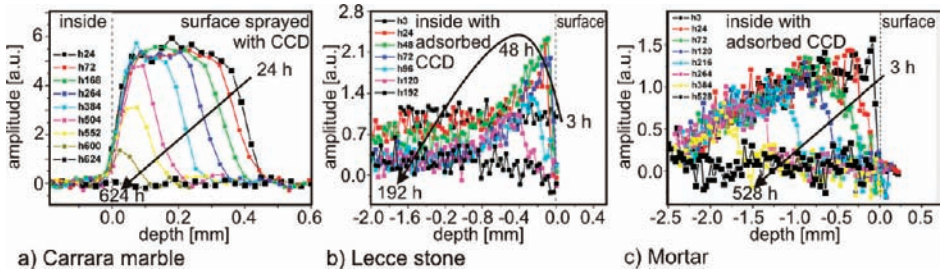

FIGURE 7. Profiles of cyclododecane solution in *n*-heptane applied on different supports. (a) Profiles collected every 24 h on the surface of a Carrara marble sample sprayed by the solution. CDD does not penetrate into the stone but forms a protective film on the surface. Initially the thickness is around 400 μm; then the film starts to sublimate and completely disappears within 624 h. (b) In Lecce stone, the substance penetrates the first two millimeters. Because of the small pore size, CDD accumulates first inside underneath the surface during the first 72 h, before it starts to sublimate. It fades away within 192 h. (c) The mortar is characterized by wider pores so the treatment penetrates the first 2.5 mm. It then sublimates beginning at the surface but remains inside the deeper lying pores for up to 528 h.

cating an inner mortar layer with higher water absorption (Figure 6f). After the measurement, a hole was cut into the wall. Inspection of the mortar layers confirmed a two-layer structure with an outer, more compact, 3 mm thick layer (Figure 6g).

Although the distributions of the transverse relaxation times from water-saturated porous media are known to be affected by an apparent shortening of the relaxation time at long times because of signal attenuation by diffusion in the inhomogeneous field of a stray-field NMR sensor, the relaxation time distributions are signatures of the material and change upon stone conservation treatment.[6] When large objects are analyzed, full fluid saturation is hard to achieve, yet the relaxation-time distributions of treated and untreated sandstone differ, indicating that the effects of stone treatment of large objects can indeed be followed by single-sided NMR. These differences are consistent with laboratory studies of partially and fully water saturated stones by single-sided NMR and NMR imaging.

3.5. Consolidants and Protectives for Porous Materials. Consolidants and protectives play a prominent role in the conservation of cultural heritage materials. The study of their interactions with the material is essential for choosing the right procedure of intervention. For example, cyclododecane ($C_{12}H_{24}$, CDD) can be both a good temporary consolidant and a protective, depending on the porosity of the materials and its method of application. It sublimates at room temperature, and its application is completely reversible. It can be used in cases of emergency that require immediate intervention or for temporary consolidation or protection of objects during transportation to the restoration site.[33] When its sublimation kinetics are known, the right time for application of the treatment can be chosen. The kinetics can be followed only by noninvasive techniques with portable instrumentation that do not interfere with the sublimation process and can be operated in situ at the artwork. The NMR-MOUSE is a suitable tool to demonstrate the efficiency of CDD as protective on nonporous materials, such as Carrara marble (porosity $\approx$ 0%) (Figure 7a), and as consolidant on materials where the porosity ranges between 35% and 40%, such as Lecce stone and mortar (Figures 7b,c). With the NMR-MOUSE, one can detect whether or not the substance has penetrated the material and how much time and even which preferential path it takes to sublimate.[34,35]

4. Challenges and Prospects

The current state of mobile and noninvasive stray-field NMR is reported and illustrated with examples from the field of cultural heritage. A comparative analysis of material properties, such as binder aging of paintings, wood density, paper quality, moisture content, and the effectiveness of conservation treatments can be conducted, where the layer structures of paintings, varnish, mortar, protectives, and consolidants can be unraveled. Such investigations are possible whenever the object contains hydrogen because the proton is the most sensitive nucleus for NMR. Magnetic components, such as steel and conducting layers, are detrimental to the measurement. A challenge are the low sensitivity and consequently long measuring times that currently restrict the use of single-sided NMR to the analysis of selected spots and excludes complete mapping of large surfaces. Also, the use of current instrumentation still requires extensive user training. As a young method, noninvasive testing by single-sided NMR is still in the development stage. It is to be expected that the detection sensitivity can still be improved, although not by orders of magnitude, that nuclei other than ^{1}H may become observable by the NMR-MOUSE, for example, ^{29}Al, which occurs in glass and ceramic ware, and that the machine-user interface will be

designed to become much more intuitive, so that less training is required to successfully use mobile NMR.

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Federico Casanova is project leader at the Institute of Technical and Macromolecular Chemistry of RWTH Aachen University. After obtaining his PhD at the University of Cordoba, Argentine, in 2001, he joined the group of Prof. Blümich as a Humboldt postdoctoral fellow to work on the implementation of imaging and flow encoding techniques in the grossly inhomogeneous fields generated by single-sided NMR sensors. His research interests are the development of suitable experimental techniques, as well as new mobile NMR sensor geometries suitable for noninvasive material characterization. He is author of more than 30 scientific papers, 4 book chapters, and several patents in the area of low-field NMR.

Juan Perlo is a research scientist at the Institute of Technical and Macromolecular Chemistry of RWTH Aachen University. He joined the group of Prof. Blümich as DAAD fellow in 2002 and obtained the PhD in Natural Sciences in 2006 working on new methods and hardware for single-sided NMR. His PhD thesis work was awarded several times at international conferences and at the university with the Friedich-Wilhem Price 2007. His research area is hardware for mobile low-field NMR. He is author of about 30 scientific publications including contributions to books and patents.

Federica Presciutti achieved her PhD in Chemistry at the University of Perugia in 2006. She is currently a postdoctoral researcher for INSTM. Her research interest is aimed to the application and development of new scientific methodologies for the study and conservation of historical artistical materials with particular attention to the implementation of NMR techniques in this field.

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Brenda Doherty obtained her PhD in Chemistry at the University of Perugia in 2007, where at present she is a postdoctoral researcher for CNR. Research interests have focused on the application and non-destructive and micro-destructive spectroscopic study of natural and synthetic consolidants for stone materials and monuments.

FOOTNOTES

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†Dedicated to the memory of Annalaura Segre.

REFERENCES

1 Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, U.K., 1961.
2 Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, U.K., 1987.
3 Haake, E. M.; Brown, R. W.; Thompson, M. R.; Venkatesan, R. *Magnetic Resonance Imaging*; Wiley-Liss: New York, 1999.
4 Dunn, K.-J.; Bergman, D. J.; Latorraca, G. A.; *Nuclear Magnetic Resonance Petrophysical and Logging Applications*; Pergamon Press: London, 2002.
5 Jackson, J. A.; Burnett, L. J.; Harmon, F. Remote (inside-out) NMR. III. Detection of nuclear magnetic resonance in a remotely produced region of homogeneous magnetic field. *J. Magn. Reson.* **1980**, *41*, 411–421.
6 Blümich, B.; Casanova, F.; Perlo, J. Mobile Single-Sided NMR. *Prog. Nucl. Magn. Reson. Spectrosc.* **2008**, *52*, 197–269.
7 McDonald, P. J.; Newling, B. Stray field magnetic resonance imaging. *Rep. Prog. Phys.* **1998**, *61*, 1441–1493.
8 Hahn, E. L. Spin echoes. *Phys. Rev.* **1950**, *80*, 580–594.
9 Carr, H. Y.; Purcell, E. M. Effects of diffusion on free precession in nuclear magnetic resonance experiments. *Phys. Rev.* **1954**, *94*, 630–638.
10 Meiboom, S.; Gill, D. Modified spin-echo method for measuring nuclear relaxation times. *Rev. Sci. Instrum.* **1958**, *29*, 688–691.
11 Eidmann, G.; Savelsberg, R.; Blümler, P.; Blümich, B. The NMR MOUSE: A mobile universal surface explorer. *J. Magn. Reson.* **1996**, *A 122*, 104–109.
12 Perlo, J.; Casanova, F.; Blümich, B. Profiles with microscopic resolution by single-sided NMR. *J. Magn. Reson.* **2005**, *176*, 64–70.
13 Perlo, J.; Casanova, F.; Blümich, B. Ex situ NMR in highly homogeneous fields: ^{1}H spectroscopy. *Science* **2007**, *315*, 1110–1112.
14 Lee, H.; Sun, E.; Ham, E. D.; Weissleder, R. Chip-NMR biosensor for detection and molecular analysis of cells. *Nat. Med.* **2008**, *14*, 869–874.
15 McDowell, A.; Fukushima, E. Ultracompact NMR: ^{1}H spectroscopy in a subkilogram magnet. *Appl. Magn. Reson.* **2008**, *35*, 185–195.
16 Blümich, B.; Mauler, J.; Haber, A.; Perlo, J.; Danieli, E.; Casanova, F. Mobile NMR for geophysical analysis and materials testing. *Pet. Sci.* **2009**, *6*, 1–7.
17 www.act-aachen.de, accessed June, 2009.
18 Song, Y.-Q.; Novel two-dimensional NMR of diffusion and relaxation for material characterization. In *NMR in Chemical Engineering*; Stapf, S., Han S., Eds.; Wiley-VCH: Weinheim, Germany, 2006; pp163−183.
19 English, A. E.; Wittal, K. P.; Joy, M. L. G.; Henkelmann, R. M. Quantitative two-dimensional time-correlation relaxometry. *Magn. Reson. Med.* **1991**, *22*, 425−434.
20 Blümich, B. *Essential NMR*; Springer: Berlin, 2005.
21 Presciutti, F.; Perlo, J.; Casanova, F.; Glöggler, S.; Miliani, C.; Blümich, B.; Brunetti, B. G.; Sgamellotti, A. Non-invasive NMR profiling of painting layers. *Appl. Phys. Let.* **2008**, *93*, 033505.
22 Daveri, A.; Clementi, C.; Presciutti, F.; Anselmi, C.; Miliani, C.; Romani, A.; Brunetti, B. G.; Sgamellotti, A. Studio dello stato di conservazione e dei materiali costitutivi

con tecniche spettoscopiche non invasive. In *L'ingegno e la Mano Restaurare il mai restaurato*; Droandi, I., Ed.; Edifir: Firenze, Italia, 2009.

23 Rosi, F.; Presciutti, F.; Clementi, C.; Miliani, C.; Sgamellotti, A. Non-invasive scientific investigation on the paintings Tutto Nero, 1956 and Bianco e Nero, 1971, The Burri Collection at Città di Castello. In *Investigation to Prevention*; Basile, G., Ed.; Gli Pri Pistoia: Pistoia, Italy, 2009.

24 Rosi, F.; Miliani, C.; Clementi, C.; Kahrim, K.; Presciutti, F.; Vagnini, M.; Manuali, V.; Daveri, A.; Cartechini, L.; Brunetti, B. G.; Sgamellotti, A. An integrated spectroscopic approach for the non invasive study of modern art materials and techniques. Unpublished work.

25 Blümich, B.; Anferova, S.; Sharma, S.; Segre, A.; Federici, C. Degradation of Historical Paper: Nondestructive Analysis by the NMR-MOUSE. *J. Magn. Reson.* **2003**, *161*, 204–209.

26 Topham, J.; McCormick, C. Ring of Truth. *The Strad*, July 2007, pp 24−30.

27 Nagyvary, J.; DiVerdi, J. A.; Owen, N. L.; Tolley, H. D. Wood used by Stradivari and Guarneri. *Nature* **2006**, *444*, 565.

28 Baias, M.; Hasenauer-Ramirez, B.; Blümich, B. Nondestructive testing of master violins and bows by portable NMR. Unpublished work.

29 Proietti, N.; Capitani, D.; Lamanna, R.; Presciutti, F.; Rossi, E.; Segre, A. L. Fresco paintings studied by unilateral NMR. *J. Magn. Reson.* **2005**, *177*, 111–117.

30 Proietti, N.; Capitani, D.; Rossi, E.; Cozzolio, S.; Segre, A. Unilateral NMR study of a XVI century frescoed wall. *J. Magn. Reson.* **2007**, *186*, 311–318.

31 Haber, A.; de Vita, A.; Del Federico, E.; Blümich, B. to be published with acknowledgement to the Paland Foundation and British School of Rome.

32 Blümich, B.; Haber, A.; Casanova, F.; Del Federico, E.; Boardman, V.; Wahl, G.; Stillitano, A.; Isolani, L. Non-invasive depth profiling of walls by portable Nuclear Magnetic Resonance, analytical and bioanalytical chemistry. In press.

33 Stein, R.; Kimmel, J.; Marincola, M.; Klemm, F. Observations on cyclododecane as a temporary consolidant for stone. *J. Am. Inst. Conserv.* **2000**, *39*, 355–369.

34 Anselmi, C.; Presciutti, F.; Doherty, B.; Miliani, C.; Brunetti, B. G.; Sgamellotti, A. The study of cyclododecane as a temporary coating for marble by NMR profilometry and FTIR reflectance spectroscopy. Unpublished work.

35 Anselmi, C.; Presciutti, F.; Doherty, B.; Miliani, C.; Brunetti, B. G.; Sgamellotti, A. The cyclododecane's behaviour within porous matrices: a non-invasive study. Unpublished work.