Chapter 5
Concepts and Applications of the NMR-MOUSE

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1 Nuclear Magnetic Resonance and the NMR-MOUSE

Nuclear magnetic resonance (NMR) is a physical resonance phenomenon utilized to investigate molecular properties of matter by irradiating atomic nuclei in magnetic fields with radio waves [1–3]. The interaction of the atomic nuclei with the magnetic field and the radio waves report about the environment of the nuclei. The nuclei are surrounded by orbiting electrons, which constitute the atoms and the chemical bonds between atoms forming molecules. Because molecules are never at rest, their motion impacts the interaction of the nuclei with the magnetic fields probed by NMR. The NMR phenomenon is put to use in many fields of science and engineering. Most notable are NMR spectroscopy for chemical analysis of molecular structures, magnetic resonance imaging (MRI) for medical diagnostics, and NMR relaxometry for testing of solid materials and fluid-filled porous media. The NMR-MOUSE (MObile Universal Surface Explorer) is a compact and portable MRI sensor for non-destructive materials testing, which measures the information of one pixel of a magnetic resonance image at a time following the principles of NMR relaxometry [4]. Among others it is of growing interest for analyzing objects of cultural heritage [3, 5–8].

1.1 Fundamentals of NMR

Eighteen grams of water contain one mole or 602,214,129,270,000,000,000,000 molecules. Although one can drink this amount in about one second, it takes

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roughly 20,000 times the age of the universe to count to this number. Thus water molecules are incredibly small. Each water molecule consists of two hydrogen atoms and one oxygen atom, and each of these atoms consists of electrons and an atomic nucleus. For such small particles the laws of classical mechanics that describe the motion of the planets and most objects of our daily life no longer apply. Instead the laws of quantum mechanics do. For a large number of elementary particles, they converge to the laws of classical mechanics.

According to the laws of quantum mechanics, many atomic nuclei appear to spin about their axes like a bicycle wheel, which when spinning stabilizes the bicycle in the gravitational field of the earth and keeps the rider from falling off. Spinning atomic nuclei are magnetic and they experience a force in a magnetic field similar to that of a wheel spinning in a gravitational field to the effect that the spinning axis rotates around the direction of the magnetic field. This rotation of the spinning axis is called precession.

The nuclei most frequently observed in cultural heritage studies are the protons, the nuclei of the hydrogen atoms. They are most abundant in the universe and give the strongest NMR signal. Typically, a percentage fraction of a mole of nuclei, for example, 10^{20} nuclei are studied by NMR. Their quantum-mechanical magnetizations sum up to a classical, macroscopic magnetization vector, which also precesses around the direction of the magnetic field ones it has been moved away from it with a radio-frequency (rf) pulse. The precession frequency $\omega = 2\pi\nu$ is measured in NMR. It is proportional to the strength B of the magnetic field,

$$\omega = \gamma B, \tag{1}$$

where the gyromagnetic ratio γ is a constant specific to the type of nucleus.

From classical mechanics one would expect that the magnetizations from all quantum-mechanical magnets in the sample would add constructively to form the macroscopic magnetization. But due to their quantum-mechanical nature, most of them add destructively and only a small fraction of the order of 10^{-5} of all protons give rise to the macroscopic magnetization at a field strength of 1 T. This is why NMR requires much more sample than optical spectroscopies to generate observable signal. But this fraction increases with field strength, so that most NMR spectrometers for chemical analysis use strong magnetic fields up to 23.5 T generated with large, superconducting magnets. High-field NMR instruments, however, are delicate, need special laboratories and trained personnel to operate. Compact NMR instruments like the NMR-MOUSE, on the other hand, use permanent magnets, have lower field strengths between 0.2 and 1.5 T, are robust, small and mobile, and much simpler to use [3–6]. The NMR-MOUSE operates near 0.5 T, about the same field strength as the first generation clinical MRI machines. At this field the precession frequency is near 20 MHz.

In NMR the precessing magnetization is measured following either of the three general ways of probing resonance. These are forced oscillations, free oscillations and noise excitation. For example, forced oscillations are invoked on a string instrument like a violin, which is played with a bow or on a wind instrument.

Free oscillations are invoked on a string instruments that is played with impulses like a guitar or a piano. White noise is usually avoided with musical instruments, because the coherent oscillations can be retrieved only by processing excitation and response in a cross- or auto-correlator. This seems cumbersome and difficult but is common practice in Fourier infrared spectroscopy, where the spectrum is the Fourier transform of an interferogram, which is the same as the autocorrelation function of the radiation transmitted through the sample. Forced and free oscillations are far more simple to understand at least to those somewhat familiar with musical instruments. When comparing sheet music for violin and piano it becomes immediately clear, that the piano is a more versatile instrument than the violin, because several tones can be played at one time compared to one or at best two with the violin. This wealth in diversity is the reason why resonance today is probed in NMR with free oscillations requiring impulses for excitation. Whereas most applications of NMR are found in diagnostic imaging and NMR spectroscopy for structure analysis of proteins [1, 2], a small but growing number of studies concern topics related to cultural heritage [9, 10].

The impulse response of a string is a vibration which decays with time. The eye sees the vibrating string and the ear hears the sound with the pitch determined by the frequency of vibration (Fig. 1a). The connection between what the eye sees and the ear hears, i.e. the connection between the time-domain oscillation $s(t)$ and frequency distribution or spectrum $S(\omega)$ is given in mathematical terms by the Fourier transformation, which decomposes the signal into a sum or integral of rotating waves $\exp\{i\omega t\}$,

$$s(t) = \int S(\omega) \exp(i\omega t)\, d\omega. \tag{2}$$

The spectrum $S(\omega)$ can be retrieved from the observed impulse response $s(t)$ by inverse Fourier transformation. For the oscillations in $s(t)$ to be observable, the magnetic field, which the nuclei see must be the same in each volume element of the sample because the magnet field strength is proportional to the precession frequency (Eq. 1). For example, if the signal is to be observable for 0.1 s, then the precession frequencies should not differ by more than 10 Hz across the sample volume of interest, which corresponds to a relative precision of 0.5×10^{-6} at 20 MHz and according to Eq. (1) defines the minimum field homogeneity of the magnet required to record NMR spectra.

Such field homogeneity is hard to achieve with permanent magnets where the sample is placed inside in the center of the magnet. It is even harder to achieve if the object to be investigated is placed in the stray-field outside the magnet. The latter situation is encountered in studies with the NMR-MOUSE. In inhomogeneous magnetic fields, an impulse response is observed from each volume element with a slightly different frequency. As a result, the sum of all impulse responses rapidly interferes to zero and often cannot be observed at all. But with a second impulse rapidly following the first one and twice as strong, the signal can be recalled in an echo and repeatedly so with a string of impulses (Fig. 1b). Such a spectroscopic

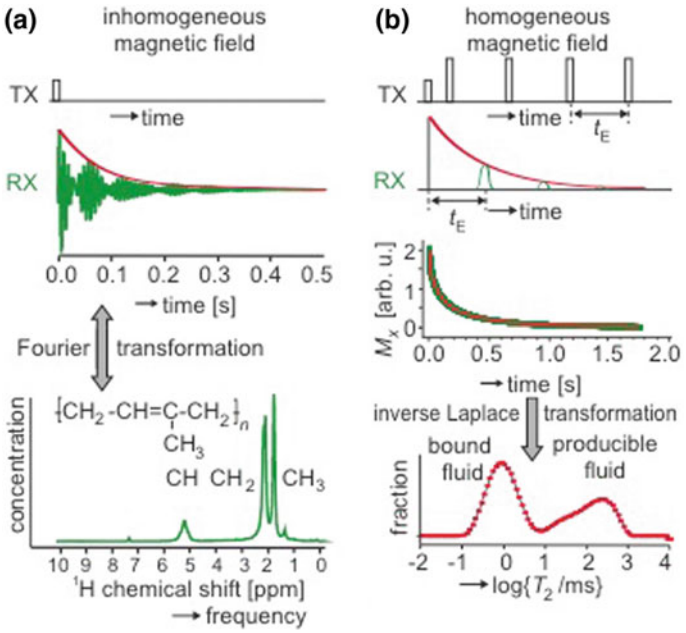

Fig. 1 NMR signals and transformations. TX denotes the transmitter sending the excitation impulses and RX the receiver recording the response signal $s(t)$. **a** Homogeneous magnetic field. Radio-frequency impulse (top), impulse response (middle) of a natural rubber solution, and corresponding Fourier transform or spectrum (bottom). **b** Inhomogeneous magnetic field. Sequence of radio-frequency impulses that generates a train of echoes (top), echo decay envelope schematic and experimental from water saturating tuff stone (middle), and distribution of relaxation times (bottom) obtained with an algorithm reminiscent of an inverse Laplace transformation

echo is not quite the same as an acoustic echo, which returns "hello" somewhat fainter when shouting "hello" into the mountains. The spectroscopic echo relates to time inversion and returns "olleh" and then "hello" when repeated again, etc. Also the amplitude of each spectroscopic echo becomes fainter, and the envelope that connects all echo maxima (Fig. 1b. middle) approximates the signal decay observed in a homogeneous magnetic field (Fig. 1a, middle). The method of observing a signal decay stroboscopicaly in an inhomogeneous magnetic field by a train of echoes is known by the initials CPMG of its inventors Carr, Purcell, Meiboom and Gill [1–3]. There are many advanced methods for measuring relaxation times, diffusion coefficients, distributions and correlation maps of these parameters [3], but the CPMG sequence is the most basic and most often used measuring scheme.

Although the information about the precession frequency is lost in an inhomogeneous field, the information about the signal decay is not. Knowledge of the precession frequency is important to the chemist, because it provides unique information about molecular structures of molecules in solution (Fig. 1a, bottom). Knowledge of the signal decay is important to the material scientist, because it

provides unique information about material properties. For example, a rapid decay on the order of 0.1 ms and less is typical for protons in rigid solids, longer decays are observed for soft solids and viscous liquids. Simple soft materials are often characterized by a single exponential decay with relaxation time T_2, complex and rigid materials show non-exponential decays. A non-exponential decays $s(t)$ can be approximated by a sum or integral of exponential decays,

$$s(t) = \int S(1/T_2)\exp\{-t/T_2\}\ \mathrm{d}(1/T_2), \tag{3}$$

where $S(1/T_2)$ is the distribution of relaxation rates $1/T_2$. Note, that on a logarithmic rate scale, the distribution of relaxation rates converts into a distribution of relaxation times by just a change of sign. This distribution can be retrieved from the observed echo envelope $s(t)$ by algorithms which are reminiscent of the inverse Laplace transformation (Fig. 1b, bottom). But other than inverse Fourier transformation, inverse Laplace-like algorithms are unstable in the presence of measurement noise, so that numerical algorithms introduce a regularization parameter which stabilizes the inversion. In many cases the use of an inversion algorithm is replaced by fitting the observed signal with a sum of two or three exponential functions,

$$s(t) = \sum_{1}^{3} S_i \exp\{-t/T_{2i}\}. \tag{4}$$

The fit parameters are the relative spin concentrations $S_i/s(0)$ and the relaxation times T_{2i}, which can be assigned, for example, to wax and water in the mortar of a wall.

The NMR relaxation time T_2 is known as the transverse relaxation time because it relates to the decay of magnetization transverse to the direction of the magnetic field. There is another relaxation time T_1, the longitudinal relaxation time. It is the time an unmagnetized sample takes to build up nuclear magnetic polarization parallel to the magnetic field once it is exposed to the field. The relaxation rates $1/T_i$ of fluids saturating the pores of porous media like rock or cement are determined by the relaxation rate $1/T_{i,\ \mathrm{bulk}}$, the surface relaxivity ρ_i, the surface to-volume-ratio S/V of the pore and the product of the self-diffusion coefficient D of the pore fluid with the internal magnetic field gradient G_{int} in the pore and the echo time t_{E} (Fig. 1b, middle). The echo time is the time between the maxima of two successive echoes in a multi-echo train. The internal field gradient results from differences in magnetic susceptibility between pore fluid and matrix material,

$$1/T_1 = 1/T_{1,\mathrm{bulk}} + \rho_1 S/V, \tag{5}$$

$$1/T_2 = 1/T_{2,\mathrm{bulk}} + \rho_2 S/V + (\gamma\, G\, t_E)^2 D. \tag{6}$$

If measured in an inhomogeneous applied field, the gradient G is the sum of both, the internal gradient G_{int} in the pore and the gradient of the applied field. Since the pore-diameter is proportional to S/V, these relationships are often

Fig. 2 The NMR-MOUSE. **a** Drawing of the sensor mounted on a displacement table for measuring depth profiles through vertical layer structures such as mortar layers covering walls. The radio-frequency (rf) coil transmits the excitation impulses and receives the signal. **b** Setup of the sensor measuring a depth profile of the natural moisture content through a painted, wet wall in the chapel of St. Mary in Chaalis

explored to approximate the pore-size distribution by the relaxation-time distribution, whereby the bulk relaxation rates and the diffusion in internal field gradients are neglected. For example, water in porous stone often gives rise to two peaks (Fig. 1b, bottom), one at short relaxation times for bound water trapped in small pores and one at longer relaxation times for water that can be exchanged by drying and wetting. In cultural heritage studies, differences in pore-size distributions can result from weathering, stone conservation treatments, as well as grain-size variations in building materials (Fig. 2).

1.2 The NMR-MOUSE

In most NMR studies, the sample rests inside the magnet, where a homogeneous magnetic field can most easily be generated. Then, however, the diameter of the magnet bore limits the sample size. Alternatively, the sample can be placed in the stray-field outside the magnet. There the sample size is not limited, but the magnetic field is usually strongly inhomogeneous. The field inhomogeneity can be tolerated if material properties are of interest which can be derived from relaxation decays. In fact, stray-field NMR is a method of non-destructive materials testing, in particular in terms of component amplitudes and relaxation times of multi-exponential decays, whereby the relaxation times $T_{2\text{eff}}$ measured in the strongly inhomogeneous field of the NMR-MOUSE are similar to the relaxation times T_2 measured in homogeneous field. Moreover, with a radio-frequency impulse only a narrow range of frequencies can be probed, which falls within the inverse duration of the excitation impulse. This translates into collecting signal with stray-field sensors, which derive from a narrow slice within the object under investigation. The NMR-MOUSE has been

designed in such a way, that this so-called sensitive slice is very flat and at a fixed distance from the surface of the sensor. Depending on the particular version of the NMR-MOUSE, the slice is 5, 10, or 25 mm away from the sensor surface, and its diameter is 10, 10, and 40 mm, respectively, with the slice thickness adjustable between 0.01 and 0.1 mm. Depth profiles covering the range from the slice distance to zero can be measured through objects by mounting the NMR-MOUSE on a computer-controlled sliding table, placing the sensor close to the object and retracting it step by step between measurements. At each position the relaxation decay is measured with a CPMG sequence, and a parameter derived from the relaxation decay is plotted versus position of the sensitive slice, in this way defining the depth profile. This parameter can be, for example, the signal amplitude, the relaxation time, a component amplitude or relaxation time (cf. Eq. 4), or a peak integral in the distribution of relaxation times. Amplitudes report concentrations, and relaxation times report material properties, for example elasticity. For noisy signals, often a weight parameter w is displayed as the profile amplitude. This parameter is the ratio of the integrals from the initial and the final parts of the relaxation decay. It is a relaxation-weighted spin density defining contrast similar to the one encountered in many medical magnetic resonance images. Depending on the position of the divide between both parts, the contrast can be optimized.

2 Selected Applications of the NMR-MOUSE

2.1 Mummies and Bones

Depending on the culture, mummies may be wrapped in textiles so that the NMR signal of mummies at a given measurement depth derives from textiles, skin, or bone. Bone consists of compact bone and of spongy bone with a cellular structure (Fig. 3c). Objectives to study mummies and bones with the NMR-MOUSE are to determine the thickness of the different textile and tissue layers, and to determine the proton density of the bone and its variation with depth.

Bone is a rigid composite material mostly from organic collagen, inorganic hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) and water. The bone density determined by ^1H NMR is organic bone density, while the bone density determined by X-ray analysis is inorganic bone density. The proton density of untreated bone indicates the state of preservation of the organic collagen matrix. Depending on the deterioration processes, organic and inorganic bone densities are not proportional to each other. Proton densities higher than in reference materials indicate the presence of other hydrogen-containing substrates such as water or conservation agents as observed, for example, in the glacier mummy Ötzi [11] and in the tibia of Charlemagne [3], respectively.

The transverse magnetization from the dry tissue of historic bone and mummies decays rapidly, and the short CPMG echo trains are analyzed with monoexponetial

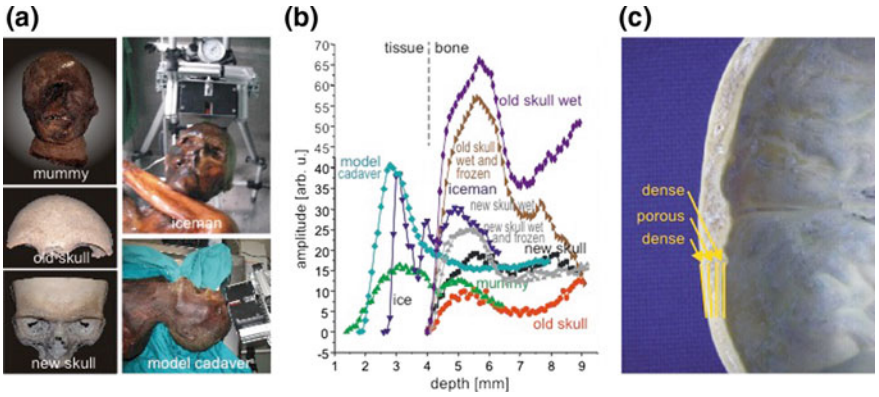

Fig. 3 Depth profiles through human foreheads. **a** Photographs showing the Egyptian mummy head, an about 1000-year-old skull excavated from the Dahlheim monastery (courtesy of Frank Rühli), a recent skull from the anatomical collection of the University of Zürich, the 5300-year-old glacier mummy Ötzi (Archeological Museum Bozen), and a model cadaver dried down to the weight of Ötzi. **b** Comparison of NMR depth profiles. **c** Bone structure of the skull. Porous bone in the center is framed by dense bone on the inside and the outside

fits or processed by calculating the relaxation-weighted spin density w from partial integrals over the echo train. Because bone is rarely flat and often heterogeneous, the signal amplitude corresponds to organic bone density only if the sensitive volume of the sensor is fully inside the bone material.

Bone degradation has been investigated in a comparative study (Fig. 3a) of signal-amplitude depth profiles (Fig. 3b) through the forehead of the Neolithic glacier mummy Ötzi in the Archeological Museum of Bozen [3, 11]. The iceman was murdered about 3250 BC near Tisenjoch in the Tyrolian Alps where his body was covered with snow and remained frozen since then until he was found in 1991. The ice-covered body is kept frozen in the museum at about −6.5 °C and 97% humidity. The depth profile through the iceman's forehead shows the layer of ice, a signal from skin and deeper down the signal from bone. Within the bone the signal first peaks and then decreases following the expected bone density variation in the forehead (Fig. 3c). Depth profiles from a well-preserved skull and a degraded skull confirm this variation of bone density. The corresponding depth profile through the forehead of a recently mummified cadaver does not show it probably because the tissue layer covering the skull bone is too thick and bone signal is not detected. On the other hand, the profile of an Egyptian mummy head shows the tissue wrapping and then the beginning of the signal from bone.

The bone signal from the iceman is somewhat higher than that of the recent skull. This is explained by liquid water in the iceman's skull based on a comparison of depth profiles through dry, wet, as well as wetted and subsequently frozen bone from the new skull and the old skull. The profiles from the new skull section wetted and subsequently frozen at −30 °C overlap and are only slightly higher than the

profile from the dry new skull. The overlap of both profiles indicates, that the water in the skull is in fact not frozen due to freezing-point depression from it's confinement to small pores. The dry profile of the old skull is significantly lower than that of the new skull, indicating lower bone density. But upon soaking it is much higher than that of the wet new skull due to water residing in the enlarged pores formed by the degradation of the bone. Moreover, the profile amplitude of the wet old skull lowers at negative Celsius temperature, because the water in the enlarged pores freezes and the signal from the solid ice decays within the deadtime of the sensor. The profile amplitude of the iceman being only slightly higher than that of the wet/frozen new skull suggest that the water in the forehead of the iceman is not frozen, and that the skull of the iceman is very well preserved.

2.2 Easel Paintings

Most easel paintings are produced on wood or canvas. Before painting, these materials are furnished with covers of other materials such as textiles and primer to provide mechanical strength and prepare the surface for painting. Paint layers consisting of pigments and binder are applied one after the other, and the final work of art is varnished to preserve it and give it a shiny finish.

Compared to other nondestructive techniques for the analysis of thin layers such as optical coherence tomography, multi-spectral imaging, and tera-Hertz spectroscopy, the depth resolution of the NMR-MOUSE is limited to about 0.01 mm [12] but the depth range can go up to 25 mm. On the other hand, the sensitive spot is a wide slice with a diameter about 10 mm. Thus the signal comes from a flat slice 1000 times thinner than wide. This requires critical alignment of the sensor parallel to the layers to be resolved. Moreover, the layers need to contain hydrogen nuclei.

The goals of studying easel paintings with the NMR-MOUSE are manifold [3, 5, 7, 8]. One goal is to characterize the softness or brittleness of the binder in terms of relaxation rates, which change with pigment type and concentration, aging, solvent exposure, storage conditions and conservation impact. Another goal is to learn about the stratigraphy of the wooden panel or canvas [12, 13]. For example, in the painting 'Adoration of the Magi' by Perugino on wood from 1470 AD reinforcing textile layers of different thickness' have been found in two positions (Fig. 4a), with the thicker one at the joint of two wooden boards. Different paint layers can only be identified in fortunate cases when the layers are sufficiently flat across the diameter of the sensitive slice. This is rarely the case with canvas paintings, because many paintings show craquelure, a network of fine cracks, which forms when the paint layers contract upon aging and the resulting flakes bend.

From a restorer's point of view, the solvent-paint interaction is of interest, in particular, the ingress of solvent when cleaning the painting and repairing damaged sections [14, 15]. In a comparative study of two 400-year-old paintings by the same

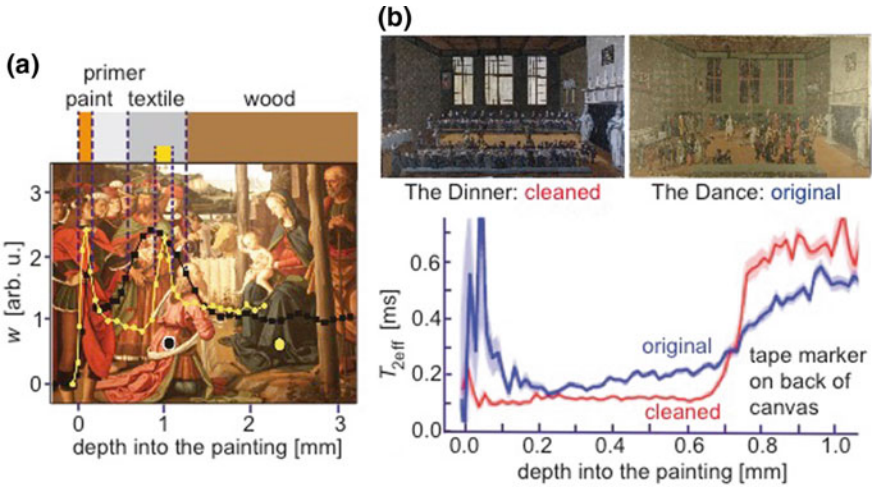

Fig. 4 Easel paintings. **a** 'Adoration of the Magi' by Perugino on wood from 1470 AD. The overlaid depth profiles collected at the two marked positions show the paint layers and the textile layers. The textile layers differ vastly in thickness. **b** The paintings 'The Dinner' and 'The Dance' from the 'Pipenpoyse Wedding' 1616, one restored and solvent cleaned, the other never restored (top) along with T_{2eff} depth profiles through the paint and canvas regions (bottom)

artist, one in its original state and the other one cleaned and restored it was found, that the T_{2eff} NMR relaxation times across the paint layer are low throughput for the restored painting, while they are higher in the lower than at the upper paint layers for the unrestored painting (Fig. 4b) [14]. Due to the fact, that low T_{2eff} indicates less mobile molecules ore more brittle material and higher T_{2eff} softer material, this observation can be explained by considering that paint binder is a multi-component mixture of molecules ranging in size from large to small. The small ones can evaporate and be washed out by solvents. The gradient in T_{2eff} across the thickness of the paint layer from the painting in its original state can be explained by evaporation of low molecular-weight molecules from the paint binder over the lifetime of 400 years of the painting. The low T_2 across the entire thickness of the cleaned painting suggests that the cleaning solvent has drained the small molecules from across the whole paint layer. This suggests, that the NMR-MOUSE is as suitable tool for optimizing solvent cleaning procedures for paintings [14, 15] and for studying drying and aging processes of paint [12]. Paint can age naturally over long times or be aged artificially in short times. To achieve the same result with artificial aging as with natural aging is extremely difficult so that NMR relaxation studies can help to examine the authenticity of a painting in question when compared to other verified paintings of the claimed artist from the same time.

2.3 Wall Paintings

Walls are painted either dry with paint containing pigments and binder or on fresh mortar using just pigments without binder. These techniques are referred to as secco and fresco, respectively. Both can be discriminated in NMR depth profiles when wetting the wall and observing the wetting and subsequent drying processes, because the binder in a secco forms a barrier to the water migration.

The pigments of a fresco are first embedded upon drawing in the calcium hydroxide forming in the reaction of lime with water. Subsequently the calcium hydroxide reacts with carbon dioxide to form calcium carbonate. To maintain a moist wall for painting for an extended period of a day's work, several thin mortar layers are applied with finer and finer grain size towards the surface. The first mortar layer is allowed to partially dry, and then further layers of the same or finer grain size follow. Each layer may vary not only in thickness, composition, and grain-size distribution, but also in the pressure applied to the uncured wet layer during plastering. Together, composition and pressure, determine the pore-space and water-absoption properties of the particular layer, and the details of the resultant layer structure are a fingerprint of the manufacturers skills and techniques.

The NMR-MOUSE provides unique information about the layer structure of frescoes by probing the moisture distribution and mobility across several layers. Moreover, preservation treatments from the past may be identified on the basis of abnormal signal strength from higher or lower hydrogen density. To measure the stratigraphy of the mortar layers from a fresco, the wall must be sufficiently wet to provide NMR signal. When not naturally wet, the wall needs to be sprayed with deionized water possibly after removing a wax layer applied in former conservation work [3, 5, 7]. From a depth profile, the thickness each resolved layer can be determined, and from the multi-echo decay envelope, component amplitudes and relaxation times can be determined either by fitting a sum of exponential functions or from the distribution of relaxation times obtained by inverse Laplace transformation. In many cases two peaks are observed in the distribution of relaxation times from water in porous media, the one at short relaxation times quantifying the amount of bound water and the one at long relaxation times the amount of free water that can be exchanged by wetting and drying. The total signal amplitude corresponding the integral of the complete relaxation-time distribution measures the total amount of water and, when scaled relative to the signal of bulk water, provides the volumetric moisture content. Correspondingly, peak integrals quantify the amounts of bound and free water (cf. Fig. 1b, bottom). Note, that when completely water saturated, the distribution of relaxation times pretty well maps the pore-size distribution unless the applied magnetic field has a strong gradient as in the case of the NMR-MOUSE. In this case, the pore size no longer scales linearly with the relaxation time [16].

Water transport through painted walls damages the painting because soluble salts are carried along, which crystallize at the surface as the water evaporates. Because the moisture flux is proportional to the moisture content, the *moisture content* is

usually taken as a first indicator for potential damage. Unless the air humidity is high, the moisture content of wet walls increases from the outside towards the inside as a result of the dynamic balance between water uptake by capillary water rise or some other source and evaporation through the wall surface [17, 18]. Such moisture-content profiles can be mapped directly and with high resolution by NMR signal-amplitude profiles. Yet the procedure is slow in contrast to other methods, none of which, however, can provide the high spatial resolution of the NMR-MOUSE. But such profiles are needed to base restoration procedures on sound engineering evidence of quantitative moisture flux, which can be obtained from modelling experimental NMR depth profiles of moisture content [19].

Moisture-content profiles are smooth as long as the wall is homogeneous. This is not so for Roman-style frescoes, which are painted on an intricate set of mortar layers with different grain sizes [19–21]. Moreover, they often have received conservation treatments with wax and other agents [20]. The stratigraphy of untreated frescoed walls in the Villa of the Papyri has been studied in Herculaneum (Fig. 5). The walls are kept at high moisture content from maintaining high air moisture in the room through evaporation of water from buckets placed on the floor to suppress water evaporation and the associated outcropping of salts from the frescoed walls (Fig. 5a). The depth profiles derived from CPMG trains reveal the mortar layer structures in terms of the moisture content, which is proportional to the signal average of the first few echoes (Fig. 5b) and in terms of the effective transverse relaxation time $T_{2\text{eff}}$ extracted from the multi-echo decays (Fig. 5c). The peaks in the amplitude profiles identify regions with high water content. The amplitude modulation with depth arises from differences in the pore spaces of the mortar layers. They are characteristic for way the wall was prepared for painting. Different craftsman or enterprises used different techniques, so that a comparative analysis of NMR depth profiles into frescoed walls opens a new window into the past of a particular fraction of the human society. It is striking that

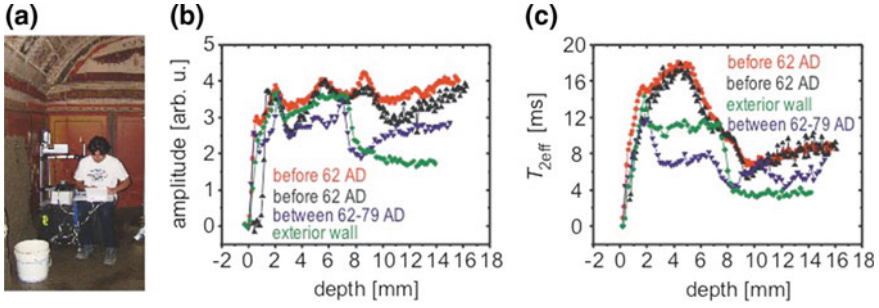

Fig. 5 Roman frescos [20]. **a** Set-up for depth profiling in the excavated room of the Villa of the Papyri in Herculaneum. **b** Moisture distribution across the mortar layers reporting the manufacturing technology and tricks of the trade from former times. **c** Distributions of relaxation times corresponding to the moisture profiles. Short relaxation times are usually characteristic for small pores, large ones for large pores

the amplitude profiles (Fig. 5b) are rather similar but that the two dating from before the earthquake in 62 AD are slightly wider than the other two, of which one is from a wall reconstructed after the earthquake and before the eruption of Mount Vesuvius in 79 AD. This suggests, that the other slightly narrower profile is also from a wall built after the earthquake.

3 Summary

Mobile NMR is not a standard analytical technique in the portfolio of art conservators and restorers because it is a comparatively young technology. From the many facets of NMR the imaging modality is of greatest interest for materials and cultural heritage studies. Mobile NMR with the NMR-MOUSE is essentially a form of one-dimensional imaging with contrast closely related to that in medical magnetic resonance imaging. The NMR-MOUSE differs from the MRI instruments used in hospitals in that it is small and portable, and its use differs in that the object rests outside the magnet and that the image is acquired pixel by pixel by physically moving a sensitive slice of the size of a small coin non-destructively through the object. The detected signal derives from hydrogen nuclei, so that hydrogen must be present in the object. Metallic or magnetic objects cannot be studied, because NMR employs magnetic fields and radio-frequency radiation.

Hydrogen nuclei are found in water and organic compounds contained in textiles, paper, leather and parchment, biological tissues, wood, wax, and many conservation agents. The NMR signal of fluids and soft matter is easiest to detect, because their CPMG decays are long, whereas the decays from hard matter like paper and varnish are short and may largely get lost during the deadtime of the instrument before they can be acquired. Therefore, porous media containing moisture can easily be analyzed by measuring the NMR signal of the fluid inside. This is the strategy when measuring depth profiles into frescoes or studying stone conservation treatments [16, 20, 22]. A similar situation is encountered when analyzing the drying of paint or solvent penetration in investigations of varnish-removal procedures for paintings or musical instruments. Wax, leather and parchment are examples of soft matter, which can well be studied by analysis of CPMG decays and more advanced two-dimensional Laplace-NMR methods [3]. The signals from wood, paper, dry paint and varnish are more demanding to measure because these materials contain only little free and bound water in addition to protons in the solid matrix material. So far the most rewarding studies with the NMR-MOUSE in the field of cultural heritage concern paint drying and solvent ingress relating to the optimization of restauration procedures for paintings, the analysis of stone and mortar to learn about their stratigraphy in the context of conservation and consolidation work, and the detection of conservation agents, wax and varnishes in frescoes, painted walls, and bones [3, 7, 8].

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