Nondestructive Testing of Objects from Cultural Heritage with NMR

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Abstract

Our world heritage is constantly facing the risk of being lost, either to severe weather conditions, chemical or biological attack, mishandling by conservators, inappropriate storage conditions, or even destruction by war. Science can provide the necessary tools for analyzing the objects of cultural heritage, assessing their state of conservation, and proposing suitable methods and strategies for preserving them for future generations. Nondestructive testing by nuclear magnetic resonance (NMR) in this area of research is relatively new. It was made possible by the development of portable single-sided NMR sensors capable of recording NMR signals from samples that are exterior to the magnet. Nondestructibility and mobility are the two main features identifying mobile NMR as an essential tool for cultural heritage research.

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Introduction

Mobile NMR sensors [1, 2] are devices that use permanent magnets to create magnetic stray fields together with surface coils attached to them to transmit and detect radiofrequency signals to and from a sensitive volume inside the sample, which is placed externally to the device. These instruments are compact and robust, but the magnetic field is inhomogeneous, limiting the number of experiments that can be executed with them. However, measurements of relaxation and diffusion parameters are little affected by the inhomogeneous magnetic field, and therefore single-sided NMR sensors can be used to determine them. Two sensors are currently being used for cultural heritage studies. They are the Bruker Profiler® [3] following the design of the original NMR-MOUSE [4] and the Profile NMR-MOUSE® [5]. Their major advantages for cultural heritage studies [6, 7] are portability of the instrument and nondestructibility of the investigation, fulfilling the condition for analysis of precious objects that need to be kept safely in museums or archeological sites and preserved intact during experiments.

There are case studies that clearly illustrate the need for portable magnets in cultural heritage studies. One such example is the analysis of Ötzi the Iceman [8], a glacial mummy, which is conserved at freezing temperature in a cold room of the South Tyrol Museum of Archaeology in Bozen, Italy. An MRI scan of Ötzi is difficult to achieve due to the right arm of the frozen body twisted sideways resulting in the need for other means of scientific investigations of this mummy. Portable and unilateral sensors, such as the NMR-MOUSE, can be used in such cases as they can be applied from one side and measure NMR parameters locally on arbitrarily large samples. This feature is also advantageous in studies at archeological sites where immobile objects, such as wall paintings and mosaics, are studied that are part of historical buildings and cannot be relocated so that the measurements have to be performed on site. Case studies where the NMR-MOUSE was used to gather information on the moisture distribution and the state of conservation of frescoes include the studies of the church of Nostra Signora del Sacro Cuore in Rome [9] and Villa Palagione in Volterra, Italy [10].

This review covers examples for the use of mobile NMR as a nondestructive tool for the analysis of objects of cultural heritage. The two mobile NMR systems used for these studies are the Profile NMR-MOUSE and the Bruker BioSpin ProFiler. Both are based on permanent magnets, whereby their open magnet geometry enables noninvasive investigations of objects of cultural heritage. The Bruker ProFiler has a comparatively thick sensitive volume suited to analyze bulk material properties, whereas the sensitive volume of the Profile NMR-MOUSE by Magritek is a thin slice suited for high-resolution depth profiling and the analysis of thin layers.

Paintings

Paintings are one of the most viewed and admired form of art present in museums, galleries, and private collections. Whether one wants to help with their conservation, restoration, or authenticity, thorough scientific investigations are in demand. A nondestructive approach is preferred throughout. Paintings have a complex multilayer structure, where a wood, canvas, metal, or ceramic serves to support the painting. This mechanical support is covered by a layer of glue and ground for sketching the outlines of the painting. A transparent “imprimitura” or the primer, to which the paint layers are applied, then covers the sketch. Several layers of paint with different pigments, binders, and glazes can be employed. The oeuvre is finally covered by a varnish layer to enrich the colors and to protect the paining [11]. By collecting information about the layered structure of the painting, one can obtain an understanding of the materials and techniques used by the artist in creating his artwork and of the procedures and changes applied in subsequent years from the impact of use and restoration. The NMR-MOUSE is the perfect tool for acquiring stratigraphy information in paintings owing to its capability of recording experiments at different depths in a sample with a depth resolution as good as 10 μm.

The possibility of using the NMR-MOUSE as a scientific tool for the nondestructive analysis of paintings had been tested on modern model easel paintings on wood prepared following the procedures of old masters. The wood panels were first covered by a layer of primer and then a paint layer from copper- and cobalt-based pigments mixed in binder [12]. Presciutti et al. used the NMR-MOUSE to gather depth profiles of these samples with a resolution of 10 μm. The different signal amplitudes can be used to differentiate between the different layers of the paintings, where the paint layer and the wood show the highest amplitudes, while the primer is characterized by smaller signal amplitude because of a lower proton density in the primer region. The NMR results were validated by scanning electron microscopy and optical microscopy. The excellent agreement between the different methods confirms that unilateral NMR can indeed be used as a tool to acquire stratigraphy information from paintings noninvasively. In addition, this study also demonstrates that the relaxation decay curves can be used to distinguish between different types of paint based on the NMR properties of the different binders and pigments used by the artists. This was demonstrated by measuring a large number of Italian Renaissance master paintings in the Galleria Nazionale dell’Umbria in Perugia, Italy. The challenge encountered when measuring the stratigraphy of paintings with the NMR-MOUSE is to align the extended sensitive slice with a diameter of about 10 mm parallel to the paint layers.

Unilateral NMR was used in combination with other analytical techniques such as portable Raman spectroscopy and visible reflectance spectroscopy to characterize the materials and state of conservation of the “Adorazione dei Magi,” a fourteenth-century painting by Bartolo di Fredi from the Pinacoteca Nazionale di Siena, Italy. Depth profiles acquired through the painting enabled the observation of three different layers – an outer layer consisting of pigment and binder, an intermediate preparatory layer, and an inner layer corresponding to the wooden panel. Depth profiles acquired at different points in the painting all indicate similar values of the NMR signal intensity of the outermost layers; however, the authors observed different intensities in the layer corresponding to the wooden panel hypothesized to be a consequence of wood degradation by the influence of physical, chemical, or biological causes [13].

Unilateral NMR is not only a tool for characterizing the layered structure of paintings and paint based on binder composition and pigment type, but it is suited to study aging and solvent treatment of painted surfaces. In their study on the impact of solvent cleaning, Fife et al. compared different techniques and materials used in the restoration of paintings. They studied two 400-year-old paintings, *The Dinner* and *The Dance*, from the *Pipenpoyse Wedding* series by the same artist; one painting (*The Dinner*) had been cleaned, while the other (*The Dance*) one remained untouched. The effective transverse relaxation time $T_{2\mathrm{eff}}$ was determined in CPMG measurements with the NMR-MOUSE, and depth profiles of $T_{2\mathrm{eff}}$ identified the differences between the two paintings. The authors showed that the $T_{2\mathrm{eff}}$ profile differed. The solvent-cleaned painting showed a constant $T_{2\mathrm{eff}}$ throughout the paint layer, whereas in the untreated painting, $T_{2\mathrm{eff}}$ increased with depth. This indicates that solvent cleaning accelerates the loss of small molecules from the binder across the entire paint layer, which occurs naturally by evaporation over the centuries only from the surface [14].

The effects of restoration techniques on paintings were investigated on painting of an angel in oil on shaped wood by Lorenzo Lippi in a study at the Opificio delle Pietre Dure in Florence, Italy. The measurements were done on three points for comparison of NMR signals between an area with maximum restoration, minimum restoration, and no restoration. Their results show, based on the high signal amplitude at larger depths, that the restoration ingredients penetrated deep in the wood. These results can help the restorer control the amount of restoration materials used on paintings such that they can minimize any damage to the original structure [15].

Differences in relaxation of paint layers are caused by the type of pigment, the type of binder, the history of aging [12], and the history of restoration. Apart from the pigments, aging and restoration impact the state of the binder by loss of small molecules and chemical changes invoked by exposure to oxidation, heat, and solvents. Neutron radiography and mobile NMR can be employed together as complementary methods for qualitative and quantitative examination of the moisture content in oil paintings on canvas when they are exposed to varying humidity conditions or in contact with liquids [16]. Due to the sensitivity of NMR relaxation to molecular mobility, the NMR-MOUSE is uniquely suited to assist in optimizing restoration procedures involving the swelling and dissolution of paint and varnish layers by solvents [17]. By the same argument, it is a unique tool to compare naturally and artificially aged paintings and help identify authentic and forged paintings.

Historical Buildings and Frescoes

Wall paintings are one of the oldest forms of art dating back to the Paleolithic era. In time, external factors, such as weather, temperature, humidity, pollution, and bacterial attack, lead to the deterioration of wall paintings. By analyzing NMR parameters such as relaxation time, diffusion coefficients, and proton density as a function of depth, the level of deterioration can be assessed. Due to the portability and open magnet geometry of the NMR-MOUSE, this information can be obtained noninvasively on site at the location of the building or fresco. Among all these factors, moisture is the one with some of the most severe long-term consequences on the structure of the building, the deterioration of the building materials, and the art decoration, such as the wall paintings and mosaics. Relevant studies from the literature were chosen to illustrate how the NMR-MOUSE was used to map the moisture content in building material and to monitor the conservation state of decorative art on building walls.

Frescoes decay due to moisture migration from alternating dryness and high humidity, failed or delayed maintenance and restoration, and other biological, chemical, and physical factors that lead to the weakening of the material, instability of the plaster, appearance of micro-cracks and strains on the surface, and concluding with their detachment.

The Bruker Profiler was employed to nondestructively assess the state of conservation of a fresco painted by Vasari in his house in Florence by mapping the T_2 relaxation times in different regions of the fresco and relating them to the structure of the supporting wall. In particular, the signature of outcropping salts and previous restoration efforts in the relaxation time distributions were analyzed. The presence of salts either in the fresco itself or in the polluted atmosphere has severe consequences to the state of a fresco because it can lead to salt crystals growing in the plaster pores that eventually change its structure and lead to crumbling of the painted surface or the appearance of a white film covering the fresco. The authors illustrate how the T_2 relaxation times can be used to assess the presence of hygroscopic salts and thus help identify suitable restoration strategies. The same study used Hahn echo experiments to analyze several regions of the painted wall and to evidence the detachment and crumbling of the painted layer from the plaster. An indication of detachment is the net decrease of the Hahn echo intensity in the detachment gap. This was ascertained by acquiring NMR signal with ProFiler inserts sensitive to different depths [18]. Alternatively, complete depth profiles can be measured with the Profile NMR-MOUSE showing the extent of the detachment [19].

Hahn echo measurements with the Bruker BioSpin NMR ProFiler also served to study the distribution of moisture in frescoes of Pellegrino degli Aretusi located in the sixteenth-century Serra Chapel of the Chiesa di Nostra Signora del Sacro Cuore in Rome. The NMR data map the two-dimensional moisture distribution of the whole painted wall on one side of the chapel. This and the study above illustrate how simple 2D Hahn echo intensity maps can help art conservators and restorers by providing quantitative maps of the moisture content in painted walls. The same study uses T_2 measurements to distinguish between regions with and without outcroppings salt. A shift in the T_2 relaxation times to longer values is a good indication for the presence of salt outcroppings. Moreover, the transverse relaxation times were also found to correlate with past cleaning and restoration works [9].

A combination of several analytical techniques, such as infrared thermography (IRT), gravimetric tests, and low-field NMR, proved to be useful in designing the restoration procedures for a deteriorated wall painting in the fifteenth-century church San Rocco in Cornaredo, Milan, Italy. The combination of methods helped acquire a detailed moisture map of the layers beneath the wall painting, portraying two regions with higher moisture content, separated by a dry area. For this study, the Bruker BioSpin NMR sensor was utilized to map an area of about 200 $\times$ 200 cm and to extract the NMR signal intensity that is proportional to the water content at a depth of 4.5–5.5 mm in the porous material within the scanned area. The NMR findings of distinct dry and wet areas are confirmed by complementary test with IRT and gravimetric. Moreover, the authors calibrated the NMR signal intensity to quantify the moisture content [20].

The presence and transport of water in historical buildings and their effect on the deterioration of wall paintings is a problem in the field of cultural heritage that requires continuous monitoring for which different complementary noninvasive techniques can be employed. Such is the case in an investigation unilateral NMR and evanescent-field dielectrometry (EFD) of the moisture distribution in an eleventh-century deteriorated wall painting of St. Clement Basilica in Rome, Italy. Different layers of the wall were investigated with the Bruker BioSpin ProFiler, in particular, the outer layer containing the painted film and deeper layers up to a depth of around 2 cm. With the help of moisture distribution maps, this method of analysis shows the effects of microbiological and chemical attack on the degradation of the wall paintings at shallow depth and at higher depth the destructive effect of water rising from the ground on the structure of the walls [21].

The intensity maps relating NMR parameters to moisture content in the pores of the painted wall are easily obtained when the moisture content is high, because high moisture content leads to a high signal intensity, which leads to a fast measurement time for quantifying the moisture content. However, if mobile NMR sensors are used to investigate dry walls, the acquisition time will be much longer due to a poor signal. This can be overcome by spraying the investigated wall with water before acquiring the NMR measurements. This technique has been employed with the Profile NMR-MOUSE to explore the layer structures of painted walls in the stateroom of Villa Palagione in Volterra, Italy, built under the Medici dynasty in 1589 [10]. This revealed an interior mortar layer, where the water content was higher, demonstrating for the first time the exceptional applicability of the NMR-MOUSE to identify multilayered mortar structures and its potential to nondestructively detect hidden wall paintings.

The NMR-MOUSE was subsequently employed to unravel the stratigraphy of decorated Roman ancient walls at Herculaneum in Italy by means of depth profiles revealing proton density transverse relaxation times and diffusion coefficients [22] at different depths at various measurement locations on the walls and from fresco fragments. The mosaic at the house of Neptune and Amphitrite was examined at different points in time to follow seasonal changes of moisture content. The results revealed the potential for further deterioration from high moisture content deeper down inside the wall and an undocumented conservation treatment of the mosaic with an organic substance, most likely wax. Depth profiles and T_2 profiles were also recorded in the walls of the House of the Black Room and the Villa of the Papyri to correlate changes in NMR parameters to different conservation treatments. Profile amplitudes revealed the stratigraphy of these walls and helped to gain insight into different conservation treatments tested on one of the walls of the House of the Black Room. Clear differences in plaster stratigraphy were detected in the walls of the Villa of the Papyri dating from before and after the earthquake of 62 AD. They encourage further studies of mortar-layer stratigraphy at different sites to learn more about the use of the houses and the workmanship and skills of the people hired to build and decorate them. Moreover, these studies show how nondestructive analyses by the NMR-MOUSE can help identify different building techniques, conservation treatments, and restoration methods of ancient walls decorated with paintings and mosaics [23].

The complementarity of NMR and terahertz time-domain imaging (THz) as measurement techniques for investigating the internal structure of wall paintings was tested on eight fresco models prepared by traditional methods. The study shows that, while THz imaging can be used to acquire high-resolution signal through the top layer of the fresco located within the first few mm, the NMR sensor can obtain stratigraphy information up to a depth of 25 mm, with a lower resolution [24].

Historical buildings deteriorate by weathering. Years of exposure to changing temperature, humidity, wind, and further biochemical factors can lead to changes in the building materials and necessitate their conservation. Relaxation-time distributions can be used as a tool to characterize the pore size distribution of fluid-saturated building materials, where short T_2 values can be used to identify small pores, while long T_2 values are attributed to large pores. Nondestructive investigations by the NMR-MOUSE can be employed to characterize the effect of treatment with stone strengtheners on the pore sizes [25]. Several studies prove the efficiency of stray-field NMR in monitoring the moisture content in building materials [26, 27]. Not only is increased moisture content in the pores a critical factor promoting the deterioration of the material but also the moisture transport. Together they form the moisture flux, which can be derived and modeled from moisture depth profiles [27]. Most conservation strategies neglect moisture transport and foot on maps of moisture content, a quantity that is easy to measure with different methods but nondestructively as a function of depth basically only by single-sided NMR. Further instrumental improvements could extend the depth range of these sensors beyond 25 mm, increase their sensitivity, and enable the recording 3D moisture maps from the walls.

Papers and Parchments

Paper is one of the oldest means of storing information and has been used for centuries to preserve historical and cultural facts for future generations. In time the paper quality degrades due to a variety of factors, such as inadequate handling and unsuitable storage conditions with exposure, for example, to humidity, extreme temperatures, chemical substances, or biological organisms such as bacteria, fungi, and insects. The common main ingredient of both historical and contemporary papers is cellulose. Whether made from long or short cellulose fibers, this organic component is rich in protons and therefore suitable for investigation by NMR. Moreover, water is present in paper in different states, either bound to the organic component or free to exchange with the environment. Unilateral NMR is an ideal method for the nondestructive analysis of paper, and ^{1}H relaxation parameters can map the deterioration state of paper by monitoring their changes from the organic component, bound and free water.

In an early research study, the use of the NMR-MOUSE for characterizing the degradation of paper was explored in measurements of the transverse relaxation of books dating from the seventeenth century. High, medium, and low stages of paper degradation could be identified, whereby increasing degradation leads to a shortening of the relaxation times of the cellulose and the water suggesting that the degradation process is associated with a loss of bound water and changes in the cellulose structure [28]. Proietti et al. mimicked the chemical aging of paper by oxidizing high-quality paper with sodium metaperiodate and monitoring the changes in relaxation times upon oxidation with the NMR-MOUSE and in low homogeneous field. The detailed analysis refers ^{13}C CP-MAS experiments and relaxation measurements in homogeneous fields proving that the nondestructive NMR technique is reliable for assessing the degradation process of paper and that the NMR-MOUSE can detect the degradation at an early stage [29].

Paper can be chemically degraded by the ink as shown in a study of iron gall ink-induced corrosion on the pages of the Codex Major, a musical anthology from the Collectio Altaempsiana (1600–1610) of Palazzo Altemps in Rome. A relative increase in the amount of the cellulose fraction with short relaxation times was detected and hypothesized to be the reason for the crumbling of the paper and to result from the acid of the ink on the fraction of amorphous cellulose with a larger amount of water molecules present in the cellulose fibers [30]. A subsequent study by spin-lattice relaxation and spin-diffusion experiments with single-sided NMR confirmed that the ink only damaged the areas locally where present and did not affect the general conservation state of the manuscript [31].

A collection of ancient manuscripts with great historical and religious importance are the *Dead Sea Scrolls* originating in the late Second Temple period. Nondestructive analyses of the structure and properties of these manuscripts are essential to ensure their good handling and preservation. Masic et al. employed the Bruker BioSpin NMR ProFiler for the measurement of longitudinal relaxation parameters, which revealed a strongly degraded collagen framework, which they hypothesized to have been caused by changes in the water fractions bound loosely and strongly to the collagen fibers or the reorganization of the water molecules in the supramolecular structures [32].

Unilateral NMR is not a stand-alone technique but should be used in combination with other methods, such as energy-dispersive X-ray fluorescence, Fourier transform infrared spectroscopy, Raman and scanning electron microscopy, and X-ray diffraction coupled with energy-dispersive spectrometry. As such the Bruker NMR ProFiler was used to analyze a Dutch map deteriorated by oxidation and dating from the eighteenth century. NMR relaxation measurements helped identify areas of the map that showed the presence of foxing and areas without foxing. In combination with other analytical techniques, the state of conservation of the cellulosic support of the map could be characterized. The influence of paramagnetic impurities on the state of preservation of the cellulosic material was evaluated, identifying Cu as an agent unfavorable to the preservation of cellulose [33].

When analyzing the factors influencing the degradation of papers and parchments, it is important to analyze not only the collagen or cellulose support but also the impact of different pigments on them. For this purpose, Del Federico et al. used unilateral NMR to understand the role played by the lead white pigment in the degradation of collagen-based binders in illuminated manuscripts on parchment. They prepared samples of solutions of binders and pigment-binder mixtures on plain microscopy slides using commercially available components. The prepared samples were analyzed using the NMR-MOUSE by extracting $T_{2\mathrm{eff}}$, the relaxation decay time in strongly inhomogeneous fields from the CPMG decay curves. The evaluation by mono-exponential fitting, inverse Laplace transformation, and multivariate data analysis consistently showed an increased $T_{2\mathrm{eff}}$ of the binder when lead white is present in the mixture due to a transition from an ordered secondary protein structure to a more mobile random coil state. These material changes are easily observed using NMR relaxation measurements and can be used as an indication for the change of the conservation state of the art materials [34].

Nondestructive analyses by mobile NMR have proven to be very useful in assessing the state of water, as well as deterioration effects in cellulose and collagen, the main ingredients of paper and parchment materials. Unilateral NMR could be further employed to evaluate the effect of different external factors and storing conditions on the conservation state of historical papers and parchments. By understanding the effects of these factors, conservation protocol can be improved to help preserve these objects for future generations.

Mummies and Bones

As early as 7000 BC, ancient civilizations preserved the bodies of their dead through mummification in preparation for their afterlife. In some cultures, the mummification was induced artificially, while in other cultures, the mummification occurred naturally resulting from extreme weather conditions. A famous naturally preserved mummy is Ötzi the Iceman, a 5,300-year-old glacier mummy found in the Alps on the border between Austria and Italy, his body being preserved for thousands of years by the low temperatures in the mountains. Rühli et al. investigated in how far different anatomical layers in mummies and bones can be discriminated with the NMR-MOUSE in a study on ancient mummies and bones, which included several Egyptian body parts such as a mummy head, a mummy hand, and a mummy finger, a Peruvian mummy, a natural mummy Ötzi the Iceman, and bones from an ancient skull and a newer skull. Often ancient mummies and bones are fragile and prone to deterioration by changes in humidity and temperature conditions, biological attack and other factors, and need to be preserved in conditioned environments to ensure optimum conservation. Being a portable instrument for nondestructive characterization, the NMR-MOUSE can be employed in the museums and at the sites where the mummies and bones are stored, such that the preservation conditions can be maintained during data collection [8].

A case study that best exemplifies these advantages of the NMR-MOUSE is the analysis of Ötzi who was investigated with the NMR-MOUSE inside the sterile cold room at the Museum of Archaeology in Bozen, Italy, where he is preserved under constant temperature and humidity conditions. In preparation of the study, the NMR-MOUSE was first tested on an isolated mummy hand for its capability to discriminate between different layers of mummy bandages versus underlying tissue and between the nail and the soft tissue in a mummy finger. In depth profiles measured through skulls of varying age, a lower proton density was observed with older skulls indicating the loss of organic matter from bone due to deterioration of its structure. In the depth profile of Ötzi, an additional layer was observed and assigned to the higher proton density of the ice layer covering Ötzi's body. In a follow-up study on bone deterioration, several tibiae were analyzed by low-field NMR. By comparing the signal amplitudes of the depth profiles recorded on an old tibia and the tibia of Charlemagne from the treasury of the Aachen Cathedral, an unusually high proton density was observed in Charlemagne's tibia and attributed to the presence of an organic preservation agent applied in former times but hitherto unknown [35]. These studies open a new and nondestructive avenue for investigating the deterioration state and past conservation efforts of mummies and bones.

Conclusions and Outlook

Nondestructive testing by unilateral NMR sensors like the NMR-MOUSE by Magritek and the Bruker BioSpin ProFiler is a comparatively new way of inspecting objects of art and objects of value to cultural heritage. The growing literature on this topic demonstrates increasing awareness of the cultural heritage community to unilateral NMR. So far the instrument has produced interesting results in a diverse range of topics concerning the nondestructive characterization historical paper and parchments, large wall paintings and mosaics, ancient mummies and bones, and valuable paintings. With single-sided NMR, one can also investigate the water content and moisture flux in historical walls and their effect on the deterioration of the building material along with the artwork covering the walls and propose strategies for combating the damaging effect of chemical, physical, and biological factors. Understanding the impact of the various factors giving rise to damage of objects of cultural heritage is an essential element when establishing protocols for their conservation. An unexpected outcome of these studies is the detection of previous conservation measures, such as the use of wax for preserving frescoes and mosaics and perhaps the tibia of Charlemagne. Moreover, unilateral NMR provides the organic bone density, which suffers first when bone deteriorates before the inorganic constituents of bone are released. For the study of paintings, unilateral NMR has the advantage in that it can provide the stratigraphy of the painting without touching it. Of particular value is the sensitivity of the NMR relaxations to solvent uptake and brittleness of the binder in paintings, enabling the optimization of solvent-based cleaning procedures for paintings. Further developments of mobile stray-field NMR instruments and measurement protocols will facilitate the use of the instrument by novices to NMR in the cultural heritage community. Improvements in the positioning systems of the NMR sensors could allow for three-dimensional scans of large objects such as paintings and frescoes producing 3D maps of NMR parameters reminiscent of magnetic resonance images albeit at lower pixel resolution.

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