DIAGNOSIS AND MONITORING OF CULTURAL HERITAGE USING A PORTABLE LOW-FIELD NMR INSTRUMENT

DIAGNOSE UND ÜBERWACHUNG DES KULTURERBES MIT EINEM TRAGBAREN NIEDERFELD-NMR-INSTRUMENT

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SUMMARY

This study presents applications of portable nuclear magnetic resonance (NMR) technology on stone and wood materials through NMR profiles. First, the results of consolidation and protection treatments with hydrophobic agents on sandstones from the cemetery of Hoppenlau, Stuttgart, are presented and discussed. The second case study focuses on measurements of the Holy Thursday altarpiece in the sacristy of Freising Cathedral. Portable NMR instrumentation was employed, demonstrating the ability of this non-invasive and non-destructive technique to characterize the porous structural properties of cultural heritage materials.

ZUSAMMENFASSUNG

In dieser Studie werden anhand von NMR-Profilen Anwendungen der portablen Kernspinresonanztechnologie (NMR) an Steinen und Holzmaterialien vorgestellt. Zunächst werden die Ergebnisse von Festigungs- und Schutzbehandlungen mit Hydrophobierungsmitteln an Sandsteinen des Hoppenlau Friedhofs in Stuttgart vorgestellt und diskutiert. Die zweite Fallstudie analysiert Messungen an einer Tafel des Gründonnerstagsretabels in der Sakristei des Freisinger Doms. Tragbare NMR-Instrumente wurden erfolgreich eingesetzt, was die Eignung dieser nicht-

invasiven und zerstörungsfreien Technik zur Charakterisierung der strukturellen Eigenschaften von Materialien des kulturellen Erbes demonstriert.

1. INTRODUCTION

Research in the field of magnetic resonance techniques applied to cultural heritage has resulted in a large body of international scientific literature, although these applications are not yet well known outside the NMR community. Today, it is possible to carry out measurements with portable instruments [1, 2] that allow non-invasive and non-destructive studies of objects of any size and of high artistic and historical value, as well as diagnosing their state of conservation. NMR relaxation times (T1 and T2) of nuclear magnetization, molecular self-diffusion (D), and their correlations can be used to investigate the structural properties of hydrogenated fluid systems for a wide variety of cultural heritage materials [3]. The main applications are the study of stone materials and the performance evaluation of new chemical compounds for the consolidation and protection of these porous materials [4-6]. Advanced two-dimensional NMR relaxometry methods enable the study of correlations between two NMR parameters, further improving the understanding of the structure of the porous space and pore connectivity. Recently, attention has turned to the study of paintings on canvas, with the aim to characterize pictorial layers and to investigate binders using low-field, portable, and completely non-invasive NMR tools [7]. NMR relaxation properties are sensitive to solvent absorption and binder brittleness in paintings, allowing the optimization of painting cleaning procedures [8]. Applications with portable instruments have also been aimed at the non-destructive characterization of frescoes and mosaics, for which studies have been carried out on the distribution of moisture content both near the surface and at different depths which reveal the characteristic mortar-layer stratigraphy underneath the surface [9].

This study presents recent applications of portable NMR technology to stone and wood materials using NMR depth profiles. In the first case study, the results of consolidation and protection treatments with hydrophobic agents on sandstone samples from the cemetery of Hoppenlau, Stuttgart, are presented and discussed. In the second case study, measurements on the Holy Thursday altarpiece in the sacristy of the Freising Cathedral, Bavaria, are analyzed.

2. EXPERIMENTAL SETUP: THE NMR-MOUSE DEVICE

In recent decades, compact devices [2] have been developed for measurements of the magnetic resonance signal in the time domain (relaxometry). Only applications of low-field NMR will be presented in this work. The NMR-MOUSE instrument (PM25, *Magritek*) has been used for all the measurements (Fig. 1).

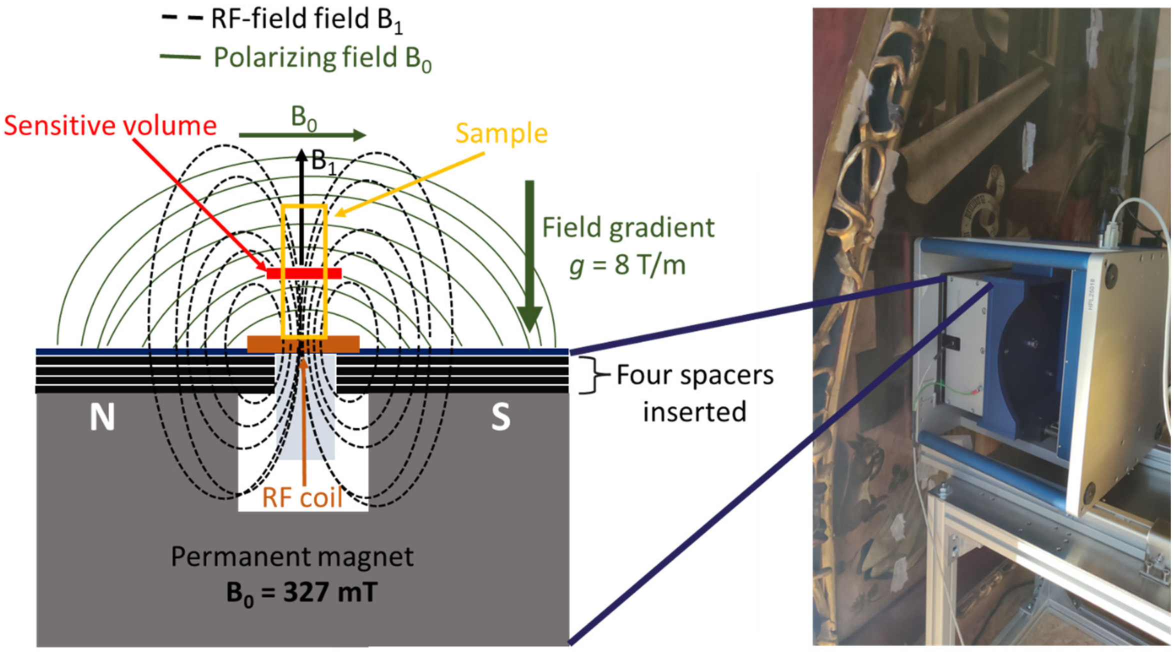

Fig. 1: Right: The NMR-MOUSE PM25 instrument by Magritek. Left: Schematic representation of the probe system that supports the sample. The B1 RF field, the static B0 polarization field, and the sensitive volume are depicted.

This instrument is a portable device for non-destructive and non-invasive *in situ* NMR measurements. It is composed of a permanent magnet that creates a static polarizing magnetic field B_0 of about 327 mT. There is also a radiofrequency (RF) coil that sends RF pulses to the sample and detects the signal related to the relaxation phenomenon. The peculiarity of this instrument is related to the position of the sample because the object under investigation is outside the magnet, unlike most NMR measurements where the sample is placed inside. This configuration leads to the presence of a strong magnetic field gradient along the direction into the sample or object. For this reason, the resonance condition is satisfied in a small region of the sample, called sensitive volume, from which the signal is acquired. A possible measurement with the NMR-MOUSE is the profile, in which the magnet is moved away from the sample, changing the position of the sensitive volume inside the sample. In this way, signal from different volumes of the sample at different depths is acquired reaching a maximum depth of 25 mm.

3. THE HOPPENLAU CEMETERY RESTORATION

Founded in 1626, Hoppenlau Cemetery is the oldest preserved cemetery in the city of Stuttgart and has been a popular place for locals and tourists since it was turned into a park in the 1960s. Due to the condition of the gravestones (mostly made of various types of sandstone), restoration work was carried out at the end of the 1980s by applying a hydrophobic agent to the gravestones. Unfortunately, in the decades that followed, this intervention accelerated the deterioration and flaking of the gravestones due to the infiltration of water into the rock and its accumulation at the interface of the hydrophobic product. It is therefore essential for the restoration to determine the depth of penetration of the hydrophobic agent, its behaviour, and the distribution of water within the porous stone structure.

3.1 Direct measure: the signal from the agents

To study the consolidation and hydrophobization characteristics, different types of treatment were simulated and studied in the laboratory using NMR. A similar hydrophobic agent to the one used in the 1980s was applied with a brush to rock samples of the same type as those used in the cemetery. Two types of consolidation agents (KSE 100 and KSE 300, Remmers GmbH, Loningen) and a hydrophobic agent (Funcosil SNL, Remmers GmbH, Loningen) were used. A total of 4 rock types were tested: Schilfsandstone (grey, porosity ~13 %), Buntsandstone (red, porosity ~8 %), and two types of Stubensandstone (yellow, porosity ~16 % and white, porosity ~10 %). The results obtained on the Schilfsandstone are presented here, because this type of stone is found most often in the Hoppenlau cemetery. First, capillary water absorption tests were carried out before treatment with a sprayer. The same tests were then repeated after the treatment to assess its effectiveness in limiting and slowing down water ingress (data not shown). The main results concern the uptake and distribution of the consolidants/protectants in the hours following the treatment itself. Fig. 2 shows the NMR profiles of Schilfsandstone after 5, 25, and 74 hours from the time of treatment.

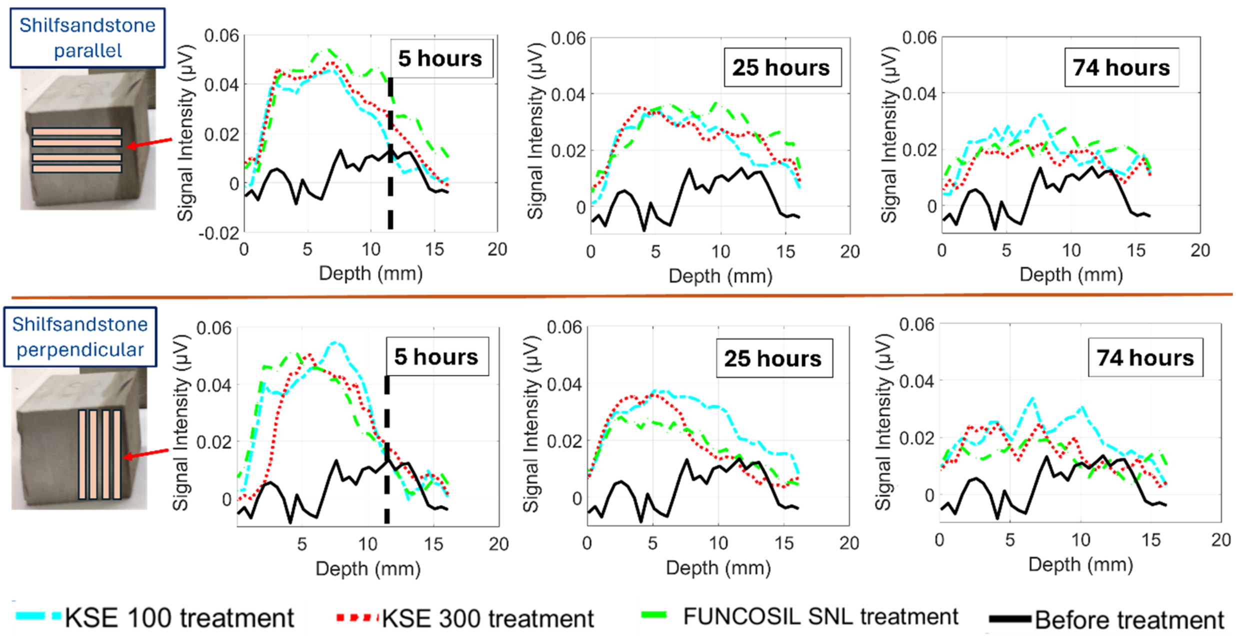

Fig. 2: NMR profiles of the two consolidants (KSE 100 and KSE 300) and the hydrophobic agent (Funcosil SNL) 5 hours (first column), 25 hours (second column), and 74 hours (third column) after treatment of the Schilfsandstone parallel to the sedimentation layers (first row) and perpendicular to them (second row). The signal Intensity is expressed in µV.

The NMR signal of the hydrogen nuclei of the agents, acquired as a function of depth in the rock (surface = 0 mm), is shown. To obtain a reference for the background noise and the amount of moisture present in the rock, the NMR signal of the rock before treatment was measured (the continuous black line around zero). In the top row of Fig. 2, the treatment was applied parallel to the rock sedimentation layers (KSE100: 82 mg/cm^2, KSE300: 100 mg/cm^2 and FuncosilSNL: 63 mg/cm^2), while in the bottom row the layers were perpendicular to the treatment (KSE100: 73 mg/cm^2, KSE300: 93 mg/cm^2 and FuncosilSNL: 47 mg/cm^2). It is interesting to compare the different absorption and diffusion behaviour of the treatment, both due to the type of consolidant/protective agent used and the orientation of the sedimentation layers. If the layers are parallel to the treatment, the rock absorbs more, and the consolidant/protective agent reaches deeper; if they are perpendicular, absorption is hindered by the alternation of the different layers. In Fig. 2, for example, 5 hours after treatment, the products reach a depth of about 11.5 mm in the perpendicular layers (perpendicular dashed line), whereas in the parallel layers Funcosil SNL and KSE 300 reach deeper (> 15 mm). It should be noted that as the hours pass, the signal from the solidifier/agent decreases dramatically due to the evaporation of the solvent: after 74 hours, the signal is more than halved. These results suggest how the in-situ NMR profile can help to follow the distribution of the product over time after treatment of, for example, the facade of a building, and to determine the depth reached.

3.2 Indirect measure: the signal from the water

In the case study of Hoppenlau Cemetery, the rocks had already been treated in the 1980s. Some samples from the cemetery were selected and the moisture content was studied as a function of distance from the outer surfaces. The results are shown in Fig. 3, which plots the NMR signal of water as a function of depth after spraying the surface with water.

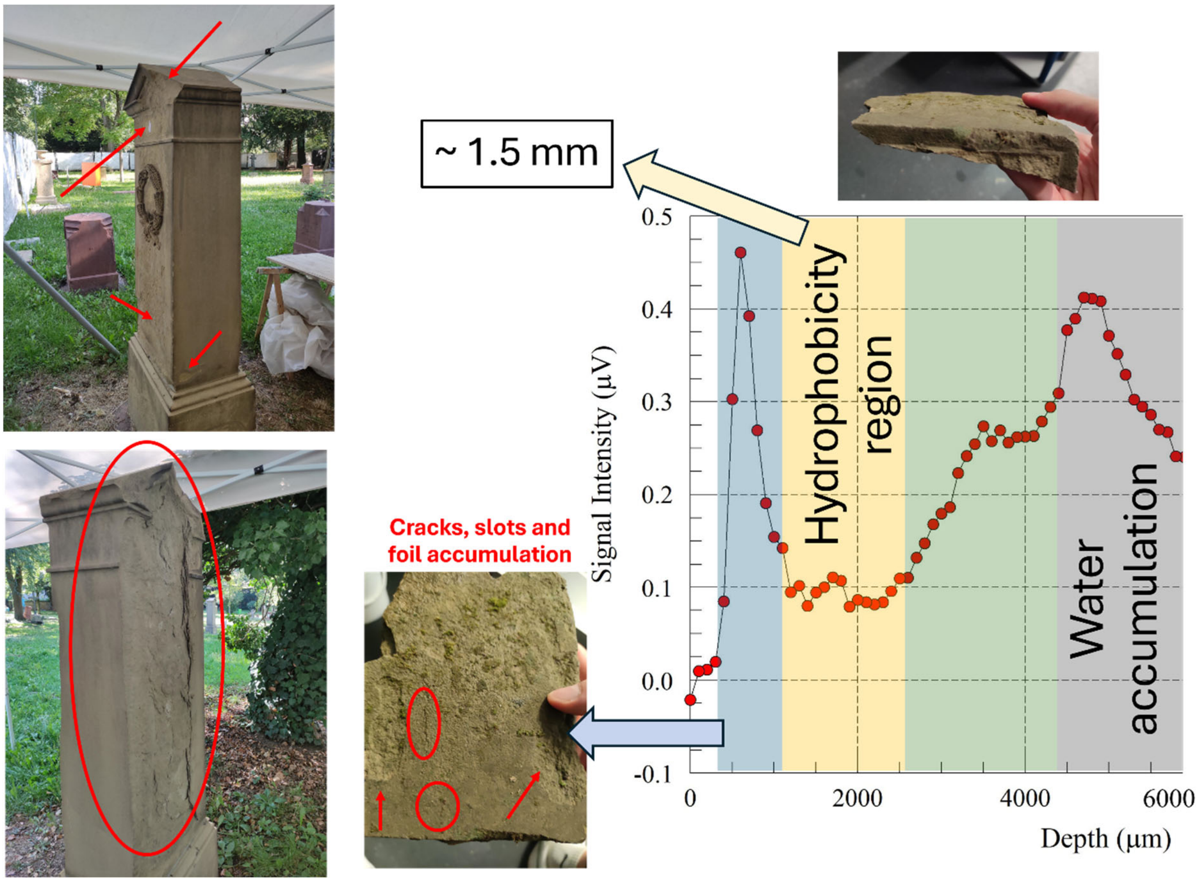

Fig. 3: Left: Two gravestones in the Hoppenlau cemetery, Stuttgart. Flaking and cracks caused by restoration work in the 1980s are visible. Right: NMR profile of a gravestone showing the hydrophobic and water-accumulation regions.

Interpretation of the profile in Fig. 3 leads to some interesting considerations. From the left, the first peak is due to the presence of small sub-surface cracks and slots through which water can infiltrate despite the surface being treated. The presence of these cracks is due to weathering over the past decades, and it is the reason why water infiltrates into the rock (as well as capillary rise from the ground). If this test had been carried out shortly after the treatment in the 1980s, it would have shown a water signal profile around zero, as all the water would have remained at the surface. Instead, today we see a peak (~0.47 µV) followed by a region of less intense signal (~0.1 µV) extending for about 1.5 mm. There we are in the region where the agent used in the past still has hydrophobic properties. Beyond the hydrophobic region, water accumulates deeper. Indeed, in the third and fourth regions from the left, the NMR signal from the hydrogen nuclei of the water increases until it reaches the area of maximum accumulation at a depth of about 5 mm. In addition to the NMR signal profile, other parameters extrapolated from the NMR measurements were used to determine the properties of the rock's porous structure in the hydrophobic region and compare them with those in the water accumulation region. An interesting result is that in the hydrophobic region there is a signal that shows much shorter relaxation times (T_1 and T_2 times) than those found in the accumulation region. In this case, the T_1 and T_2 relaxation times are an indication of the amount of water trapped in the pores of the stone matrix. In a fully water saturated porous material, the shorter the T_1 and T_2 parameters, the smaller the pore size in which the water is confined. Therefore, the presence of shorter T_1 and T_2 in the hydrophobic area can be interpreted by a reduced pore size due to the presence of the hydrophobic product being distributed on the pore surfaces (as well as by a lower water content than in the fully saturated condition). This information can be crucial in planning and implementing an appropriate restoration strategy.

4. THE HOLY THURSDAY ALTARPIECE RESTORATION

In the sacristy of Freising Cathedral in Bavaria is the Holy Thursday altarpiece painted by Hans Mair von Landshut in 1495 (Fig. 4). Dr. Weniger (Bavarian National Museum) describes it as *the most important pre-Baroque altarpiece preserved in Freising and one of the highest quality, late Gothic pictorial groups in old Bavaria*. In recent decades, the painting has deteriorated (e.g. shrinkage) due to the unsuitable temperature and humidity conditions in the sacristy. In 2016, it was removed from the wall and a climate-controlled room was created inside the sacristy for its restoration and to re-increase the moisture content in the wood.

Fig. 4: The Holy Thursday altarpiece, kept in the sacristy of Freising Cathedral in Bavaria.

One of the main problems faced by the restorers is to understand the flow and volumetric concentration of humidity in the different layers of the painting, physical conditions necessary to plan appropriate conservation measures. With some difficulty due to a low signal-to-noise ratio (since in this case it is obviously not possible to increase the moisture content and thus the signal by wetting the surface with water), NMR was able to provide important information. The measurements (non-invasive and non-destructive) were carried out directly in situ, both on the back and on the front of the painting.

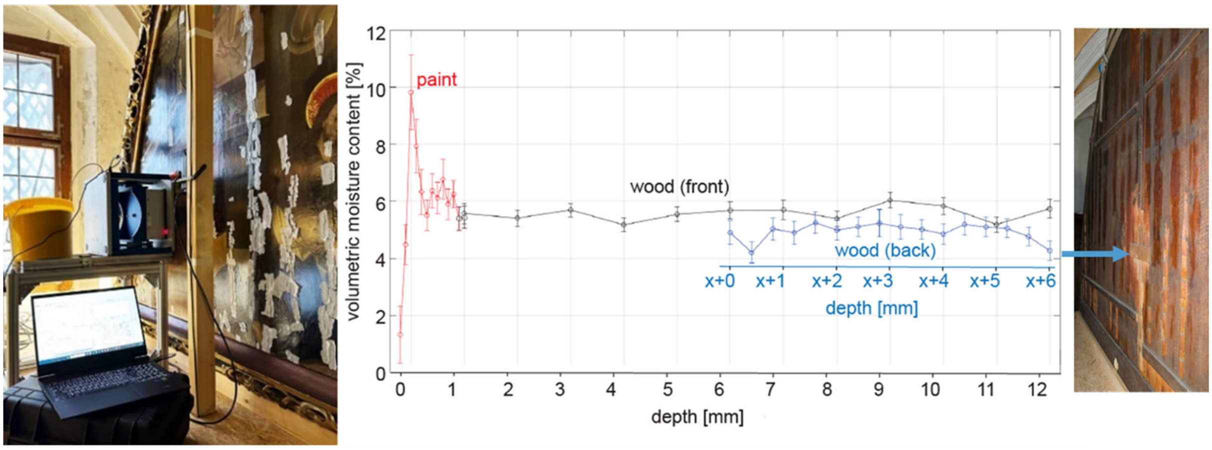

Fig. 5: Left: Portable low-field NMR instrument (NMR-MOUSE PM25) used in the investigation of the painting. Right: NMR depth profile showing volumetric profile of moisture content in the wooden board, valuable information for conservation treatments.

The instrument (Fig. 5, left) is compact and portable, allowing it to be positioned directly in the regions of interest. The graph in Fig. 5 shows the trend of the volumetric percentage of moisture content as a function of depth in the painting. Relaxation times were analyzed to identify and separate the paint layer from the underlying wood layer. The graph on the right refers to measurements made on the wood at the back of the painting (x represents the distance to the front of the painting and it is approximately 14 mm, the total thickness is approximately 20 mm). The first item to note is the initial peak in the painting, due to both high moisture content and the presence of paint material that could contribute to the NMR signal. In addition, the wood measured at the back of the painting has a lower moisture content (within the measurement error) than the wood near the painted front. This could be due to two factors: the moisture in the wood close to the facade cannot as readily evaporate because of the layer of paint; and the fact that the wood on the back has been treated during the restoration to preserve it. The T_2 relaxation-time profile in the paint layer was also calculated and showed interesting features which require further measurements to interpret and relate to the stratigraphy.

5. CONCLUSIONS

In this work, applications of portable nuclear magnetic resonance instrumentation demonstrate the capabilities of non-invasive and non-destructive techniques in characterising porous structural properties of materials of interest to cultural heritage. The moisture content of stone and wood materials, as well as the penetration capabilities of conservation products, have been characterised to assess the effectiveness of treatments and the state of conservation and to aid the design and implementation of restoration interventions. NMR relaxometric profiling technique is an innovative candidate for obtaining important information for *in situ* diagnostics and monitoring.

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