Analyzing the Porosity Distribution in Stone Surfaces by Means of Unilateral NMR after Long-Term Outdoor Weathering

Melanie Groh 1,* , Jeanette Orlowsky 1, and Robert Schulte Holthausen 2

1 Chair of Building Materials, TU Dortmund University, August-Schmidt-Str. 8, 44227 Dortmund, Germany; jeanette.orlowsky@tu-dortmund.de
2 Ardex GmbH, Friedrich-Ebert-Straße 45, 58453 Witten-Annen, Germany; robert.schulte.holthausen@rwth-aachen.de
* Correspondence: melanie.groh@tu-dortmund.de; Tel.: +49-231-755-6006

Abstract: Porosity changes in the near-surface area of sandstones due to long-term weathering can produce deterioration. Therefore, porosity analyses on weathered sandstones are significant for detecting possible influences on the pore structure. Classical methods for determining the porosity and pore size distribution in sandstones can only investigate the entire sample volume. In contrast, in this publication, the porosity was analysed in 0.2 mm steps over a depth of 5 mm by means of single-sided NMR measurements on water-saturated sandstones under vacuum. Evaluations of Obernkirchener and Schleeriether Sandstones that were weathered outdoors in Germany for over 30 years are presented. The results showed that the water content in Vol.-% strongly correlated with the normalised NMR signal. The unweathered sandstones showed a uniform distribution of micro and capillary pores throughout the stone depth. As a result of 30 years of outdoor weathering, changes in the pore structure occurred at the sandstone surface due to weathering down to depths of about 0.6 mm. The porosity of the Schleeriether Sandstone samples, mainly the microporosity, clearly increased in this region. Due to the dominance of capillary pores in the Obernkirchener Sandstone, the changes were not as pronounced, but a shift towards smaller pores in the surface area was observable.

Keywords: unilateral NMR; natural stone; long-term weathering; porosity distribution; porosity changes

1. Introduction

Natural stones are exposed to a variety of external weathering influences over their usage as a building material. Depending on the petrographic and petrophysical properties of the natural stones, environmental factors influence their weathering intensity over time. This can also change the existing stone properties and produce deterioration. In particular, the pore structure of natural stones due to weathering phenomena, especially in the near-surface regions, is of decisive importance with regard to water absorption behaviour and pollutant ingress.

Analysis of the pore structure of mineral building materials is conventionally carried out using mercury porosimetry and additional microscopic transillumination of thin sections [1,2]. Furthermore, investigations using the NMR technique produced successful porosity analyses of concrete samples [3,4]. The study presented in this paper was intended to evaluate the extent to which nuclear magnetic resonance spectroscopy could be used as a non-destructive measuring method to evaluate the depth-dependent detection of the porosity distribution and changes in weathered natural stones.

2. Materials and Methods

From 1985 to 1996, a BMFT (Federal Ministry of Research and Technology, Bonn, Germany) Priority Programme focused on the decay and conservation of natural stones.
In this context, several outdoor field studies were conducted to analyse the weathering processes of different stone materials by considering their influencing factors, as well as testing suitable protective agents on the samples. One of these studies was launched by the Zollern Institute (today: Deutsches Bergbau-Museum Bochum) in the year 1986/1987. In this study, several natural sedimentary stones were exposed at different weathering locations in Germany (three sites each in North Rhine-Westphalia and Bavaria) for up to 30 years. The used sample material consisted mainly of sandstones and limestones, which are frequently used as building materials but also have a comparatively high susceptibility to weathering [5,6].

Two representative stone types of the outdoor field study were Obernkirchner (OKS) and Schleeriether Sandstones (SST), which were used for the investigations in this study. The beige-to-yellowish-grey Obernkirchner Sandstone can, for example, be found as a load-bearing building material in sacred buildings, such as the Willibrordi Cathedral in Wesel and partly in the Royal Palace in Amsterdam. Nowadays, it is increasingly used for facade panels. Schleeriether Sandstone is a light-green-to-grey sandstone and is often used in the Bavarian region for solid constructions, such as the Würzburg Residence, but also for structuring elements on facades, sculptures and monuments [7].

Table 1 summarises the petrographic and petrophysical properties of both of these stone types. The microstructure of OKS is characterised by solid grain-to-grain and sutured contacts and kaolinite is included as a pore space filler. Its weathering resistance is considered very good to good. In addition to discoloration, biogenic growth and black crusts, the weathering phenomena of the Obernkirchner are rarely scaling and spalling. The clayey-chloritic matrix of SST contains punctate and elongated grain contacts and the grains are mostly covered with chlorite. Overall, the weathering resistance of Schleeriether Sandstone is classified as moderate to good. Due to outdoor weathering, discoloration, sanding, crumbling and occasional flaking occur in protected areas. After longer exposition times, scaling and salt damage, especially in the base areas, can be observed [2,7].

| Stone Type | Obernkirchner Sandstone (OKS) | Schleeriether Sandstone (SST) |
|------------|-------------------------------|-------------------------------|
| Characterisation [7] | Fine-grained, well-sorted quartzitic sandstone | Fine-grained, moderately sorted sandstone |
| Mineral content [1,2] | Quartz 85%, rock fragments 10%, muscovite 5% | Quartz 65%, rock fragments 20%, muscovite 10%, feldspar 5% |
| Matrix [7] | Quartzitic, kaolinitic | Clayey-chloritic |
| Weathering damage [7] | Black crusts, spalling | Scaling, sanding, salt damage |
| Total porosity (%) | 20 | 21 |
| Average pore radius (µm) | 3.4 | 6.0 |
| Water absorption coefficient (kg/(m² × h⁰.⁵)) | 1.38 | 2.17 |

The test specimens for the field study had a triangular prismatic shape to simulate typical conditions on buildings. A part of the samples was impregnated with organosilicon-based hydrophobing agents before exposition, while the other samples remained untreated [5]. The untreated samples exposed in Eifel, Nuremberg and Kempten were the focus of this study (Table 2). A detailed description of the climatic data and pollutant values at the weathering locations over the last 10 years of exposure can be found in Or-
Overall, Nuremberg had a lower number of hours with relative humidity above 80% than the other two locations. In contrast, the pollutant input was the highest in Nuremberg (urban area) compared with the others. At the test locations, the specimens were placed 1 m above the ground on a metal frame (Figure 1, left). Two years after the exposition, a 3 cm thick slice was cut off each prism and afterwards stored indoors. After 24 resp. 30 years of natural weathering of the remaining prisms, the samples were removed and a second slice was cut off the other side. Additional samples were stored indoors as references. In order to carry out various measurements on the samples in the laboratory [10,11], the slices were cut into several sample sections and used for individual investigations (Figure 1, top right).

Table 2. Used stone types and their exposition.

| Stone Type                  | Exposure Site | Exposition Time   |
|-----------------------------|---------------|-------------------|
| Obernkirchener Sandstone (OKS) | Indoors       | -                 |
|                             | Eifel         | 2 and 24 years    |
|                             | Nuremberg     | 2 and 30 years    |
|                             | Kempten       | 2 and 30 years    |
| Schleeriether Sandstone (SST) | Indoors       | -                 |
|                             | Eifel         | 2 and 24 years    |
|                             | Nuremberg     | 2 and 30 years    |
|                             | Kempten       | 2 and 30 years    |

The samples considered in this study already showed darkening of the surface and biogenic growth after 2 years of weathering. These damage patterns increased only slightly over the course of the long-term exposure (Figure 1, bottom right). Overall, macroscopic and microscopic examinations of other sample sections of the two stone types showed a considerable change in appearance due to long-term weathering, with the Schleeriether Sandstone showing less color change over the exposition time. The analysed black and covering weathering layers on the surfaces consisted of accumulated particles on existing biofilms (more pronounced growth in terms of height for the Obernkirchener Sandstone samples). By means of XRD investigations, different types of salts (especially sulfates...
and nitrates) and, to a lesser extent, carbonates were confirmed as present in the surface deposits of the Schleeriether Sandstone samples [1,2].

In order to be able to analyse the possible structural changes in the near-surface area of the samples due to the outdoor weathering, different investigation methods were used.

2.1. Mercury Porosimetry

One of the most common methods for determining the pore volume, pore size distribution and total porosity of natural stones, besides gas adsorption, is mercury porosimetry according to DIN ISO 15901-1 [8]. For this purpose, sample material (pieces with a size of approx. 5 mm × 5 mm) was taken from the area near the surface (in the first 4–5 mm) of samples section 2. The stone fragments were dried at 40 °C until a constant mass was reached. The drying process was carried out as gently as possible in order to prevent temperature-sensitive stone components from being affected and subsequently falsifying the measurement results. After that, they were stored in an exsiccator until they were measured.

The measuring method using mercury is based on the non-wetting property of this heavy metal (contact angle between 125° and 150°). Under vacuum, mercury is pressed through the pore entrance into the open pore space. In this process, the applied pressure is inversely proportional to the pore inlet radius. Assuming that all pores are cylindrical capillaries, the pore size distribution can be determined using the Washburn equation [12].

Thus, this measuring method detects the pore spaces that are accessible for possible transport processes of liquids or gases. The pore entrance radius, as the connecting point of interconnected pores, is of decisive importance and this value is measured with the mercury porosimetry [13,14].

According to Klopfer [15], pores of building materials can be divided into three categories: micropores: <0.1 μm, capillary pores: 0.1 μm ≤ d < 1000 μm and macropores: ≥1000 μm. Micropores, which are responsible for diffusion transport and capillary condensation, can be detected via mercury porosimetry down to a minimum pore diameter of approx. 0.008 μm (according to the manufacturer’s specifications of the measuring device used: Pascal 140–240 Porosimeter from the company Porotec). The relevant capillary pore fraction of these sandstone types, which is important for capillary and water vapour diffusion transport, can be recorded entirely with the dilatometer (CD 6) used for the measurement because pore diameters of up to 100 μm can be detected with it.

Thus, in Figure 2, the pore size distribution of the Schleeriether and Obernkirchner Sandstone samples revealed that both types of stone contained micropores, as well as capillary pores. However, a higher proportion of micropores was present in the Schleeriether Sandstone samples. Furthermore, the average pore diameter was larger than for the Obernkirchner samples.

![Figure 2. Pore size distribution of the Obernkirchner and Schleeriether Sandstones stored indoors (reference).](image-url)
2.2. NMR Measurements

To obtain a non-destructive statement about the water and porosity distribution of the investigated material, measurements were carried out by using a unilateral NMR device (Profile NMR-Mouse®, PM 25) [16,17]. A single-sided inhomogeneous stray field, which is set up by four permanent magnets, aligns the atomic nuclei (1H) of water inside the sample in the field’s direction. By emitting high-frequency pulses (sent from a coil placed between the permanent magnets) during the measurement, the atomic nuclei are deflected within a measuring volume of roughly 40 mm × 40 mm × 0.2 mm and their response is detected [18].

The received response is transmitted to a spectrometer (Kea2) and visualised via data processing software in the form of unitless diagrams. Individual depth-dependent amplitudes (A) and relaxation times (T2) can be extracted from the recorded decay curves. Thus, a detected decay curve always consists of several individual exponential functions, which can be assigned to the different types of pores present in the samples. The separation of the individual signals takes place either through a multi-exponential fit or inverse Laplace transformation [4,19]. Further information on the detected number of relaxation components and the method of curve fitting used for the available sample material follows in Section 3.

In order to determine the most suitable measurement parameters for the available samples, several preliminary tests were carried out. The measurement parameters derived from the preliminary investigations are listed in Table 3.

Table 3. Measurement parameters and adjusted values.

| Measured Parameter               | Adjusted Value |
|----------------------------------|----------------|
| OKS                             | SST            |
| Resolution (µm)                 | 200            | 200            |
| Repetition time (ms)             | 850            | 850            |
| Pulse length (µs)                | 16             | 16             |
| Echo time (µs)                   | 80             | 80             |
| Number of echoes                 | 100            | 100            |
| Number of scans                  | 200            | 200            |
| Measuring depth from sample surface (µm) | 4800  | 4800 |

The relaxation signals measured with the unilateral NMR device are always relative values without quantitative reference and are subject to measurement-dependent deviations and scattering. Since the quantitative content of water within the samples needed to be determined in this work in order to derive the existing porosity and distribution, pure water was used for the previous standardisation [3,18,20]. The deviations of the first echoes were corrected (correction factor 1. echo = 0.75) and the resulting corrected amplitudes were normalised to the amplitude of pure water (A_w = 2.26, T_{2w} = 104 ms).

In order to obtain sufficiently precise information about the penetration behaviour of water into the mineral surface structure of the investigated natural stones, the test specimens were prepared accordingly. In order to identify different saturation levels, the dry samples (stored in a room climate) were first stored under water at atmospheric pressure (1 bar) for 7 days according to DIN EN 13755 [21] (Figure 3, top left). To avoid surface effects that prevent the further filling of pores in the sample depth, as described in Bortolotti et al. [22], the specimens were subsequently exposed to a negative pressure of 0.05 bar for a period of 13 days (Figure 3, bottom left). For each storage period, a sample was taken out of the water bath and prepared for measuring. First, the excess surface water was blotted off and a 1 mm thick glass plate was placed on the weathered surface. Then, the sample was wrapped in a one-layer vapour-tight polyethylene film and placed with the weathered side downwards on the NMR device (Figure 3, right). The glass plate prevented direct contact between the film and the sample surface, which separated the
barely distinguishable NMR signals from the plastic film and material and allowed for the sample surface to be detected more accurately [4].

Figure 3. Top left: storage of the samples under water at atmospheric pressure (1 bar) for 7 days. Bottom left: then, the samples were stored at negative pressure (0.05 bar) for 13 days. Right: measuring the relaxation times after each storage period with the unilateral NMR device.

3. Results

To evaluate the amount of water absorbed by each sample during the different storage conditions, their weight was determined gravimetrically before each NMR measurement (Figure 4). After the analysis of the 13-day vacuum-saturated samples, they were put back into the water and stored there for more than 1 year (on average, a total of 378 additional days) for a long-term study.

Figure 4. Water ingress of Obernkirchener and Schleeriether Sandstone samples over successive storage methods. Mean values of the different outdoor exposures (see Table 2).

Comparing the gravimetrically determined water uptake of the two stone types after the first 7 days of water storage (1 bar), the exposed Schleeriether Sandstone (SST) samples recorded higher values than the Obernkirchener Sandstone (OKS) samples. The application of negative pressure (0.05 bar) during underwater storage caused a stronger water ingress in the Obernkirchener samples than in the Schleeriether samples such that a similar level was reached after 13 days. In addition, the Obernkirchener samples showed a further increase as a result of long-term exposure to water. In comparison, the water absorption of the
unweathered (indoor) samples of both stone types showed related percentage increases. The exposition time of 24/30 years had no influence on the water uptake of the Obernkirchener Sandstones. Only the long-term-exposed Schleeriether samples had an increased uptake compared with the samples exposed only for 2 years.

The results of the destructive gravimetric method showing incomplete saturation after only water saturation were further confirmed via depth profiles of the unilateral NMR measurements (based on the measured relaxation curves corrected with the given parameters and normalised to the amplitude of pure water), which additionally allowed for depth-dependent statements to be made about the water distribution within the samples (Figure 5). For example, the high amplitude values in the first 400 µm of the 7-day water-stored Obernkirchener reference sample indicated a water enrichment in this near-surface area, whereas lower values were present at a greater depth (4000 µm). In the case of the Schleeriether Sandstone sample, more water had penetrated the sample depth during the saturation with 1 bar, which could be recognised by the higher amplitude values there. Thus, the Schleeriether Sandstone showed a less pronounced surface effect. As a result of the saturation under vacuum, the surface effects disappeared, which led to an equalisation of the amplitude values in the sample. In the deeper layers, higher signal amplitudes were achieved than with standard pressure (1 bar), which reached a constant level throughout the depth.

![Figure 5. Depth profiles at different saturation levels for unweathered Obernkirchener and Schleeriether Sandstones.](image)

Based on the gravimetrically determined water absorption values, the porosity of the individual samples could be calculated according to DIN EN 772-4 [23]. Thus, the generated values for the samples saturated using negative pressure (Vac 13d) reflected the open porosity of each sample. The comparison of the gravimetric water absorption values with the measured and normalised NMR signals (averaged over the entire depth of the samples considered) at the different saturation levels showed a positive linear correlation with minimal scattering due to the natural internal stone heterogeneity (Figure 6). Similar results were generated for both stone types for saturation under atmospheric pressure (W 7d) and under vacuum (Vac 13d). Overall, a shift due to slightly higher normalised NMR amplitude values, especially for the Schleeriether Sandstone samples, could be detected. This may have resulted from detected amplitude signals due to residual stone moisture in the dry state (storage at room climate) of the samples (for SST-dry: \( A/A_w \approx 2.5 \text{ Vol.-%} \), for OKS-dry: \( A/A_w \approx 0.9 \text{ Vol.-%} \); see Figure 5—dry samples). When the samples were exposed to water for more than a year, comparatively higher NMR signals were obtained for both stone types, with almost constant gravimetric water absorption values. A possible influence on the results due to different degrees of weathering of the samples was not detectable. Overall, this showed once more that this NMR measuring method is well suited for determining the porosity of different natural stone types [24].
In order to obtain further information from the measured exponential relaxation curves about the existing porosity, as well as different pore sizes in individual depths of the samples, a curve fitting was performed by means of a multi-exponential fit [4]. Based on the two types of pores present in the investigated sample material listed in Section 2, which were detected using mercury porosimetry, two relaxation components were assumed, and thus, a bi-exponential fit was used for the evaluation.

The individual $T_2$ relaxation times generated from the decay curves depend on the properties of the pore surfaces and provide information about the pore sizes [25]. Thus, the component with the shorter $T_2$ relaxation time ($T_{2-1}$) indicates the detection of pores with small radii, in this case, micropores. The corresponding amplitude values ($A_1$) provide information about the present quantity of micropores at the depth considered in each case. The capillary pores are detected via a longer $T_2$ relaxation time ($T_{2-2}$) and in accordance with the $A_2$ amplitude values.

As Figure 7 shows, the unweathered sandstone samples of both stone types saturated under vacuum showed a constant porosity distribution over the entire measuring depth of 4800 µm. Despite the approximately equal total porosity of both types of stone, quantitative differences in the present types of pores could be determined. One-third of an average Schleeriether Sandstone sample consisted of micropores, while in the Obernkirchen samples, the capillary pore fraction dominated the pore structure. This correlated with the pore size distribution of the two stone types measured using mercury porosimetry (see Figure 2).

**Figure 6.** Correlation of gravimetric water uptake and measured NMR signal normalised to $A_w$.

**Figure 7.** Fitted and stacked relaxation depth profiles of unweathered Obernkirchen and Schleeriether Sandstone samples saturated under vacuum (0.05 bar).
The determination of the porosity using NMR showed lower values than those measured using mercury porosimetry for almost all Schleeriether Sandstone samples (except the samples exposed in Nuremberg) (Figure 8). When the samples were stored in water for more than one year, the NMR values became more and more similar to those obtained with mercury porosimetry. However, since the correlation coefficient regarding water uptake decreased as a result of long-term saturation and such saturation periods are unusual, even for laboratory conditions, the saturation of the samples by means of 0.05 bar negative pressure was still taken as the relevant condition for the detection of porosity. The determination of the porosity by means of gravimetric water uptake showed somewhat lower values for all samples in comparison to the porosities determined using NMR, which correlated with the results presented in Figure 6. Based on the comparison of the pore types present, an increase in micropores on the surface could be observed, especially for the long-term weathered samples exposed in Nuremberg and Kempten. Despite the existing scatter of the measured values due to natural internal stone heterogeneities (for example, indoor storage over 2 and 30 years), similar distributions were found for all samples exposed for 2 years.

![Figure 8](image_url)  
**Figure 8.** Distribution of micro (A1) and capillary (A2) pores within the Schleeriether Sandstone samples that were measured in the near-surface area (400 µm) and the sample depth (4000 µm), and presentation of the resulting NMR-porosity ($\Phi_{\text{NMR}}$) (averaged over the entire depth of the samples) in comparison with the detected porosity measured using mercury porosimetry ($\Phi_{\text{Hg-Poro}}$) and gravimetric water uptake ($\Phi_{\text{grav. WA}}$).

A similar curve progression after 2 years of exposure was also detected for the Nuremberg samples when the distribution was plotted over the measured sample depth (Figure 9). However, after long-term outdoor weathering, an increase in the micro and capillary porosities could be observed in the first 600 µm. Thus, the NMR-porosity at a sample depth of 200 µm increased from 19 Vol.-% (2 years) to 38 Vol.-% (30 years) due to superficial weathering phenomena. The sample material weathered in Kempten showed a similar, but slightly lower, porosity change at the surface.
Figure 8. Distribution of micro (A1) and capillary (A2) pores within the Schleeriether Sandstone samples that were measured in the near-surface area (400 µm) and the sample depth (4000 µm), and presentation of the resulting NMR-porosity ($\Phi_{\text{NMR}}$) (averaged over the entire depth of the samples) in comparison with the detected porosity measured using mercury porosimetry ($\Phi_{\text{Hg-Poro}}$) and gravimetric water uptake ($\Phi_{\text{grav.-WA}}$).

A similar curve progression after 2 years of exposure was also detected for the Nu-
remberg samples when the distribution was plotted over the measured sample depth (Figure 9). However, after long-term outdoor weathering, an increase in the micro and capillary porosities could be observed in the first 600 µm. Thus, the NMR-porosity at a sample depth of 200 µm increased from 19 Vol.-% (2 years) to 38 Vol.-% (30 years) due to super-
ficial weathering phenomena. The sample material weathered in Kempten showed a sim-
ilar, but slightly lower, porosity change at the surface.

Figure 9. Fitted and stacked relaxation depth profile of the 2- and 30-year weathered Schleeriether Sandstone samples (exposure site: Nuremberg) saturated under vacuum (0.05 bar).

Comparing the NMR-porosity of the Obernkirchener samples with the results using mercury porosimetry, lower values for almost all samples were detected again, while the porosities, determined using water uptake, showed similar results to the measured NMR-
porosities (Figure 10). Overall, the distribution of the two pore types detected showed mainly capillary pores in the Obernkirchener Sandstone samples, which had already been observed in the indoor samples. In particular, within the sample depth, no microporosity was found. Furthermore, a larger scattering of porosities of the individual samples was noticed. Nevertheless, a slight shift towards smaller pore sizes was seen on the surface (400 µm) of the exposed samples as a result of outdoor weathering, which increased somewhat over the long-term exposure (Figure 11).

Figure 10. Distribution of micro (A1) and capillary (A2) pores within the Obernkirchener Sandstone samples measured in the near-surface area (400 µm) and the sample depth (4000 µm), and presentation of the resulting NMR-porosity ($\Phi_{\text{NMR}}$) (averaged over the entire depth of the samples) in comparison with the detected porosity measured using mercury porosimetry ($\Phi_{\text{Hg-Poro}}$) and gravimetric water uptake ($\Phi_{\text{grav.-WA}}$).
Comparing the NMR-porosity of the Obernkirchener samples with the results using mercury porosimetry, lower values for almost all samples were detected again, while the porosities, determined using water uptake, showed similar results to the measured NMR-porosities (Figure 10). Overall, the distribution of the two pore types detected showed mainly capillary pores in the Obernkirchener Sandstone samples, which had already been observed in the indoor samples. In particular, within the sample depth, no microporosity was found. Furthermore, a larger scattering of porosities of the individual samples was noticed. Nevertheless, a slight shift towards smaller pore sizes was seen on the surface (400 µm) of the exposed samples as a result of outdoor weathering, which increased somewhat over the long-term exposure (Figure 11).

Figure 10. Distribution of micro (A1) and capillary (A2) pores within the Obernkirchener Sandstone samples measured in the near-surface area (400 µm) and the sample depth (4000 µm), and presentation of the resulting NMR-porosity ($\Phi_{\text{NMR}}$) (averaged over the entire depth of the samples) in comparison with the detected porosity measured using mercury porosimetry ($\Phi_{\text{Hg-Poro}}$) and gravimetric water uptake ($\Phi_{\text{grav. WA}}$).

Figure 11. Fitted and stacked relaxation depth profile of the 2- and 30-year weathered Obernkirchener Sandstone samples (exposure site: Nuremberg) saturated under vacuum (0.05 bar).

4. Comparison and Discussion

In this study, unilateral nuclear-magnetic resonance was used to gain non-destructive information about the pore size distribution in the near-surface regions of long-term-weathered natural stones. To classify the results and to compare them with conventional destructive measuring methods, the corrected and normalised NMR signals were correlated with the gravimetrically determined water absorption. The linear positive correlation coefficient reconfirmed the results of previous studies on mineral building materials, showing that the NMR-porosity ($\Phi_{\text{NMR}}$) is a direct measure of the waterfilled porosity of the investigated sample [20]. An influence of the correlation coefficient towards higher NMR signals may result from detected amplitude signals due to residual stone moisture in the dry state of the samples not accounted for in the gravimetric testing.

Due to the required sampling down to depths of about 5 mm for mercury porosimetry, this method cannot be used for a depth-resolved observation of changes in porosity due to weathering. However, these measurements can be made with the NMR method presented here, for which a bi-exponential fit for elevation was used. In order to make a suitable assumption about the number of components present within the samples, it is necessary to consider in advance which samples are involved and which types of pores are to be expected. The examined stone types showed a different distribution of the two types of pores present, which had an influence on the analyses. While the Schleeriether Sandstone had both micro and capillary pores, the capillary pores dominated in the Obernkirchener sandstone. The evaluation of the pore fractions over a stone depth of 5 mm in 0.2 mm steps showed no change in porosity over the depth of the Schleeriether Sandstone in the unweathered state. Outdoor weathering over 30 years in southern Germany caused an increase in porosity at the stone surface down to about a 0.6 mm stone depth, especially for the micropores. However, in the case of Obernkirchener Sandstone, a change in porosity at the stone surface as a result of 30 years of outdoor weathering could not be clearly determined; the capillary porosity tended to decrease at the surface after long-term weathering, while the microporosity increased up to 2 Vol.-%. This could indicate possible densification of the pore spaces at the surface due to covering weathering layers and a reduction in superficially accessible kaolinitic pore space fillings, which was determined on the basis of polarisation microscopy images of other long-term exposed Obernkirchener samples [2]. Further investigations have to be carried out in this regard.

Due to the much larger measurement volume and the possibility of measuring a wide range of different pore radii and sample depths, the results of the NMR measuring method are subject to less scatter than those determined by means of mercury porosimetry.
5. Conclusions and Outlook

Overall, the non-destructive measuring method used showed good suitability for the detection of the porosity at individual sample depths. Changes in the pore structure could be determined, especially when comparing different exposure durations. The results presented, which were determined on sandstones that were water-saturated under vacuum, can be summarised in the following key points:

- The Obernkirchener and Schleeriether Sandstones showed a uniform water content over the whole stone depth (measured in 0.2 mm steps) due to saturation under negative pressure (0.05 bar).
- The gravimetrically determined water absorption (in Vol.-%) correlated with the measured NMR signal normalised to $A_w$ (in Vol.-%).
- Using a bi-exponential fit of the $T_2$ decay curve, the micro and capillary pores that were present in the two sandstones could be distinguished.
- The unweathered sandstones showed no change in porosity distribution over the sample depth, measured in 0.2 mm steps to a 4.8 mm depth. While the Schleeriether Sandstone had 6 Vol.-% micropores and 12 Vol.-% capillary pores, the Obernkirchener Sandstone had only 1 Vol.-% micropores and around 18 Vol.-% capillary pores.
- As a result of 30 years of outdoor weathering in southern Germany, the proportion of pores of the Schleeriether stone surface (the first 0.6 mm) and the permeability of water increased.
- As a result of 30 years of outdoor weathering, the change in the pore structure of the Obernkirchener Sandstone was not as well observable. The proportion of capillary pores on the surface of the stone samples tended to decrease, while the micropores at a stone depth of 0.4 mm increased to about 2 Vol.-% for all exposure sites.

In the next steps, the results will be verified by further comparative investigations, such as microscopic examinations. Furthermore, this method for porosity analysis should also be adapted for hydrophobic long-term-weathered natural stone samples. This could provide a good basis for establishing single-sided NMR as a non-destructive measuring system to carry out in situ porosity measurements of building structures.

Author Contributions: Conceptualisation, M.G., J.O. and R.S.H.; methodology, M.G., J.O. and R.S.H.; validation, M.G. and J.O.; formal analysis, M.G. and J.O.; investigation, M.G.; data curation, R.S.H.; writing—original draft preparation, M.G.; writing—review and editing, J.O. and R.S.H.; visualisation, M.G.; supervision, J.O.; project administration, J.O.; funding acquisition, J.O. All authors have read and agreed to the published version of the manuscript.

Funding: This work was performed as part of a project funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), project number 496342862.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: We would like to thank Stefan Brüggerhoff and the Zollern-Institute, Deutsches Bergbau-Museum Bochum, who initiated this project within the framework of the BMFT research project “deterioration of stone-conservation of stone” for providing the stone samples for our investigations. We acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References
1. Braun, F. Zur Ermittlung des Langzeitverhaltens hydrophobierter Natursteinoberflächen unter dem Einfluss der Natürlichen Verwitterung. Ph.D. Thesis, TU Dortmund University, Dortmund, Germany, 2021. [CrossRef]
2. Braun, F.; Orlowsky, J.; Brüggerhoff, S. Analyzing near-surface regions of hydrophobic and long-term weathered natural stones at microscopic scale. *J. Herit.* 2020, 3, 457–473. [CrossRef]
3. Schulte Holthausen, R.; Raupach, M. Monitoring the internal swelling in cementitious mortars with single-sided $^1$H nuclear magnetic resonance. Cem. Concr. Res. 2018, 111, 138–146. [CrossRef]
4. Schulte Holthausen, R.; Raupach, M.; Merkel, M.; Breit, W. Zerstörungsfreie Bestimmung der Auslaugung von Beton mittels einseitiger Wasserstoff-Kernspinresonanz. Bautech 2020, 97, 679–687. [CrossRef]
5. Brüggerhoff, S.; Wagener-Lohse, C. Gesteinsverwitterung in Freilandversuchsfeldern–Erfahrungen mit ihrer Errichtung und Nutzung. Bautenschutz Bauanw. 1989, 12, 76–80.
6. Mirwald, P.W. Umweltbedingte Gesteinszerstörung untersucht mittels Freilandverwitterungsexperimenten. Bautenschutz Bauanw. 1986, 24–27.
7. Grimm, W.-D. Bildatlas Wichtiger Denkmalgesteine der Bundesrepublik Deutschland, Teil II: Bildband; 2. Erweiterte Auflage; Ebner Verlag: Ulm, Germany, 2018; ISBN 978-3-87188-247-0.
8. DIN ISO 15901-1:2019-03; Evaluation of Pore Size Distribution and Porosity of Solid Materials by Mercury Porosimetry and Gas Adsorption–Part 1: Mercury Porosimetry (ISO 15901-1:2016). Beuth Verlag GmbH: Berlin, Germany, 2019.
9. DIN EN 15801:2010-04; Conservation of Cultural Property–Test Methods–Determination of Water Absorption by Capillarity; German Version EN 15801:2009. Beuth Verlag GmbH: Berlin, Germany, 2010.
10. Orlowsky, J.; Braun, F.; Groh, M. The influence of 30 years outdoor weathering on the durability of hydrophobic agents applied on Obernkirchener Sandstones. J. Build. 2020, 10, 18. [CrossRef]
11. Braun, F.; Orlowsky, J. Single-sided NMR Experiments on hydrophobic and long-term weathered natural stones. Monument Future–Decay and Conservation of Stone. In Proceedings of the 14th International Congress on the Deterioration and Conservation of Stone, University of Göttingen and University of Kassel, Göttingen, Germany, 7–12 September 2020; Siegesmund, S., Middendorf, B., Eds.; Mitteldeutscher Verlag: Halle, Germany, 2020; pp. 633–638. ISBN 978-3-96311-172-3.
12. Washburn, E.W. The dynamics of capillary flow. Phys. Res. 1921, 17, 273–283. [CrossRef]
13. Giesche, H. Mercury porosimetry: A general (practical) overview. Part. Part. Syst. Charact. 2006, 23, 9–19. [CrossRef]
14. Engelhardt, W.V.; Pitter, H. Über die Zusammenhänge zwischen Porosität, Permeabilität und Korngröße bei Sanden und Sandsteinen. Heidelb. Beträge Mineral. Petrogr. 1951, 2, 477–491. [CrossRef]
15. Klopf, H. Feuchte. In Lehrbuch der Bauphysik: Schall, Wärme, Feuchte, Licht, Brand. Teil 1 einer Baukonstruktionslehre; Lutz, P., Jenisch, R., Klopf, H., Freymuth, H., Krampf, L., Eds.; B. G. Teubner: Stuttgart, Germany, 1985; pp. 265–434. ISBN 3-519-05014-5.
16. Casanova, F.; Perlo, J.; Blümich, B. Single-Sided NMR; Casanova, F., Perlo, J., Blümich, B., Eds.; Springer: Berlin/Heidelberg, Germany, 2011; ISBN 978-3-642-16306-7.
17. Braun, F.; Orlowsky, J. Non-destructive detection of the efficiency of long-term weathered hydrophobic natural stones using single-sided NMR. J. Cult. Herit. 2020, 41, 51–60. [CrossRef]
18. Schulte Holthausen, R.; Raupach, M. Influence of fresh concrete pressure on cover porosity investigated by single-sided proton nuclear magnetic resonance. Mag. Concr. Res. 2021, 73, 45–54. [CrossRef]
19. Weichold, O.; Hutt, S.; Keine, S.; Schulte Holthausen, R. Non-destructive moisture measurement in building materials using single-sided nuclear magnetic resonance. In Proceedings of the International RILEM Conference on Materials, Systems and Structures in Civil Engineering–Conference Segment on Moisture, Technical University of Denmark, Lyngby, Denmark, 22–24 August 2016.
20. Schulte Holthausen, R.; Raupach, M. Determination of porosity and pore size distribution in concrete by single-sided $^1$H NMR–From white cement pastes to grey cement mortars. In Proceedings of the IBAUSIL, Weimar, Germany, 12–14 September 2018; Ludwig, H.M., Ed.; F.A. Finger-Institut für Baustoffkunde, Bauhaus Universität Weimar: Weimar, Germany, 2018.
21. DIN EN 13755:2008. Beuth Verlag GmbH: Berlin, Germany, 2008.
22. Bortolotti, V.; Camaiti, M.; Casieri, C.; De Luca, F.; Fantazzini, P.; Tenerzi, C. Water absorption kinetics in different wettability conditions studied at pore and sample scales in porous media by NMR with portable single-sided and laboratory imaging devices. J. Magn. Reson. 2006, 181, 287–295. [CrossRef] [PubMed]
23. DIN EN 772-4:1998–10; Methods of Test for Masonry Units–Part 4: Determination of Real and Bulk Density and of Total and Open Porosity for Natural Stone Masonry Units. German version EN 772-4:1998. Beuth Verlag GmbH: Berlin, Germany, 1998.
24. Keine, S.; Schulte Holthausen, R.; Raupach, M. Single-sided NMR as a non-destructive method for quality evaluation of hydrophobic treatments on natural stones. J. Cult. Herit. 2019, 36, 128–134. [CrossRef]
25. Antons, U. Untersuchungen zur Dauerhaftigkeit Hydrophober Schichten im Beton Mittels NMR. Ph.D. Thesis, RWTH Aachen University, Aachen, Germany, 2017.