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NMR Techniques for Non-Destructive Investigations of Historical Stone Artefacts

Mara Camaiti
CNR, Institute for Conservation and Enhancement of Cultural Heritage, Sesto Fiorentino (Florence), Italy

Paola Fantazzini
University of Bologna, Department of Physics, Bologna, Italy

Mirko Gombia
University of Bologna, Department DICMA, Bologna, Italy

ABSTRACT: Magnetic Resonance Imaging (MRI), a rapid and noninvasive diagnostic technique, has been successfully applied to study both the capillary properties of some rocks (travertine, Lecce stone, and Matera stone), and the performances of some polymeric treatments (acrylic polymers and silica gel) used for the conservation of historical stone artifacts. MRI applied to stone materials is based on the detection of the ^{1}H nuclei of liquid water inside the pore spaces of the rock, which allows the visualization of the liquid water diffused in treated or untreated stone samples. For the treated samples the localization of water absorbed gives indirectly the spatial distribution and efficacy of the polymer into the rock.

1 INTRODUCTION

The restoration and conservation treatments of historical stone objects as well as monumental buildings are usually performed by applying polymeric compounds having hydrophobic and often cohesive properties. The water-repellent characteristic is required for avoiding direct contact between the rock and liquid water, the main deterioration agent. Cohesive properties, on the other hand, are necessary to restore the mechanical characteristics of the decayed stone.

The efficacy and durability of the conservation treatments depend on the characteristics of the compounds used, but they are also highly influenced by the penetration and homogeneous distribution of the polymeric product into the structure. A high probability of pore blockage occurs when low penetration depth and/or non-homogenous distribution of macromolecules into the stone are obtained, and the significant reduction of pore space in the superficial layers of the rock can cause further deterioration in consequence of environmental stress.

The evaluation of distribution and penetration depth, therefore, is a basic condition for understanding the conservation properties of polymeric treatments and settling the better application techniques in different stone materials.

Magnetic Resonance Imaging (MRI) and Magnetic Resonance Relaxometry (MRR) have been proved to be valid non-destructive techniques for evaluating these parameters (Appolonia et al. 2001, Borgia et al. 2003a, b, c). MRI, a spatially-resolved NMR technique, allows indirectly visualizing the distribution of hydrophobic products through the detection of liquid water. MRR, a non spatially-resolved technique, detects the changes in the capillary properties of the stone, by comparing the relaxation time distributions of the confined water before and after the treatment with hydrophobic products. In situ relaxation measurements are also possible, and a direct correlation between the MR-images and the relaxation time distributions has been found: the distribution of liquid water inside the stone at different water-uptake times, in fact, is in agreement with the changes observed in the relaxation time distributions (Camaiti et al. 2005).

In this work a systematic investigation of the water capillary uptake of different stone materials (Lecce stone, Matera stone, and travertine) has been carried out by MRI in order to evaluate the influence of the porosity (total porosity and pore size distribution) on the performance of the protective/consolidating agents. The performances of some polymeric products most widely used for the restoration/conservation of stone Cultural Heritage (Paraloid B72 (PB 72) and ethyl silicate (W-OH)) have been tested.

Different application methods, as well as products having different molecular weights, have been also investigated, proving that MRI gives additional and more important information on the polymer distribution than traditional or destructive methods.

2 MATERIALS AND METHODS

2.1 Images acquisition

MRI measurements were performed at room temperature by a tomograph ARTOSCAN^{TM} (Esaote S.p.A., Genova, Italy), consisting of a 0.2T permanent magnet (10mT/m maximum gradient intensity), corresponding to 8MHz for protons. The high quality of low-field MRI quantitative measurements has already been shown by Borgia et al. (1996). Multi-slice Spin-echo sequences were used to obtain 10 axial sections on each sample (slice thickness = 5 mm, gap between slices = 1mm, pixel size = 0.78 x 0.78 mm^2, number of excitations 8, TR = 900 ms, TE = 10 ms). Particular care was devoted to avoid electronic saturation of the signal and to guarantee that the signal intensity was determined on the same dynamic range for all samples.

The MR-images were acquired after the stone samples were left in water capillary absorption through the untreated face for a fixed time (1h, 3h, 5h, 24h or 7 days). The water capillary absorption test was carried out in accordance to the UNI 10859 method (2000) and the procedure followed for the MRI analysis is reported in Borgia et al. (2000).

2.2 Stone sample

Three lithotypes, having the same chemical composition but different porosity, were chosen: travertine, Lecce stone, and Matera stone. Travertine and Lecce stone were quarry samples, while Matera stone samples were decayed and came from a hypogeum located in Matera (Italy).

Lecce stone, a biocalcarenite with 32-34% of total porosity, was cut in prismatic samples of dimensions 5x5x2 cm^3. Treatments were carried out on one 5x5 cm^2 face by brush or by capillary absorption following the procedure reported in Borgia et al. (2000).

Travertine is a calcareous rock with very compact regions (total porosity 1-5%) alternated to zones having large pores (up to several millimetres). Sample dimensions were 5x5x2 cm^3. The treatment was carried out on one 5x5 cm^2 face by brush.

Matera stone, a biocalcarenite having 40-43% of total porosity, was also cut in prismatic samples of dimensions 5x5x2 cm^3. In order to evaluate the penetration properties of consolidating agents in presence of previous treatments, PB 72 was first applied and then, after 32 months, ethyl silicate. Both the treatments were carried out by brush on one 5x5 cm^2 face.

In all the cases the amount of polymer applied on each sample was determined by weighing the sample after evaporation of the solvent or curing of the product (treatment with ethyl silicate).

2.3 Polymeric products

Two polymeric products were used for treatments: Paraloid B-72 and ethyl silicate, widely used in the conservation of stone artefacts.

Paraloid B-72, poly (ethyl methacrylate-co-methyl acrylate) 70/30, from Röhm & Haas has glass transition temperature (Tg) = 43°C and average molecular weight (Mw) = 90500 amu. The polymer was applied on Lecce stone and Matera stone as chloroform or acetone solutions. The concentration of the solutions, the applications methods and the amount of effective product applied are reported in Table 1.

Ethyl silicate from CTS-Italy was applied as supplied by the producer on Lecce stone, travertine and Matera stone (Table 1). After the treatment, the stone samples were cured at room conditions (20°C and 60% RH) for 1 month before drying in a $CaCl_2$ desiccators and proceed to the MRI measurements.

Table 1 : Treatments conditions of the stone samples investigated.

Lithotype	Polymer	Solvent	Solution concentration (w/w)	Application method	Amount of product applied g/m^2	Amount of product applied g/100g stone
Lecce stone	PB 72	Chloroform	1 %	brush	28	0.074
Lecce stone	PB 72	Chloroform	1 %	capillary absorption (6h)	76	0.190
Lecce stone	W-OH	Methoxy propanol / white spirit	75%	brush	315	0.814
Travertine	W-OH	Methoxy propanol / white spirit	75%	brush	81	0.164
Matera stone	PB 72 +	Acetone	7.5%	brush	152	0.497
	W-OH	Methoxy propanol / white spirit	75%	brush	119	0.388

Molecular weight distributions were carried out by a modular SEC system using a RI detector and two PL Gel mixed D columns 30 cm length, 5 μm particle size, for the separation. Chloroform was used as mobile phase and standards of poly(methyl methacrylate) for the calibration.

3 RESULTS AND DISCUSSION

3.1 Capillary properties of rocks

The MRI technique allows the visualization of the presence and the spatial distribution of the ^1H nuclei of liquid water inside porous materials. Different porosity as well as different water capillary absorption properties of rocks may be well evidenced by the MR images of sections within the selected samples and are represented by zones with different detectable proton densities (zones more or less bright). The images reported in Figs. 1-3 show these differences in three not treated lithotypes (travertine, Lecce stone and Matera stone).

In the travertine sample, even if large pores are present, the mass of water absorbed after short (1h) as well as after long times (7 days) of contact with liquid water is low (less than 1.4g). The MR images of the same slice within the sample at different water absorption times show a localization of water in two thin layers, proving the poor homogeneity of the rock with zones “wetter” than others and then more liable to deterioration than the “dryer” ones (Fig. 1).

A higher homogeneity, apart the presence of a shell evidenced at the bottom of the images, is detected in Lecce stone (Fig. 2). The kinetics of water absorption shows a gradual water uptake and diffusion inside the pores of the rock. A higher mass of water (7-8 times) is also absorbed by the Lecce stone sample in comparison with the travertine one, both at short and at long times.

A different behaviour is observed for Matera stone (Fig. 3), where the presence of a “hollow” is visible, but the kinetics of water absorption is faster than in the other lithotypes: after 1h of water capillary absorption the mass of water was the 92% of the amount at 7 days (14.5g compared with 15.7g at 7 days).

3.2 Performance of the polymeric materials

Porosity and pore size distribution influence not only the water capillary absorption, but also the penetration depth and the distribution of the polymeric compounds used as protective or consolidating agents. As known, the higher the penetration depth and the more uniform the distribution of the polymers, the more effective is the treatment. By MRI it is possible to visualize the spatial distribution of liquid water in the stone and provide direct evidence of the extent and localization of the polymeric materials (hydrophobic products).

Travertine treated with ethyl silicate shows a drastic reduction of the water capillary uptake, and the MR images of the same section within the sample appear dark also after 7 days of water absorption (Fig. 4), which is evidence for a uniform distribution of the product in the whole sample.

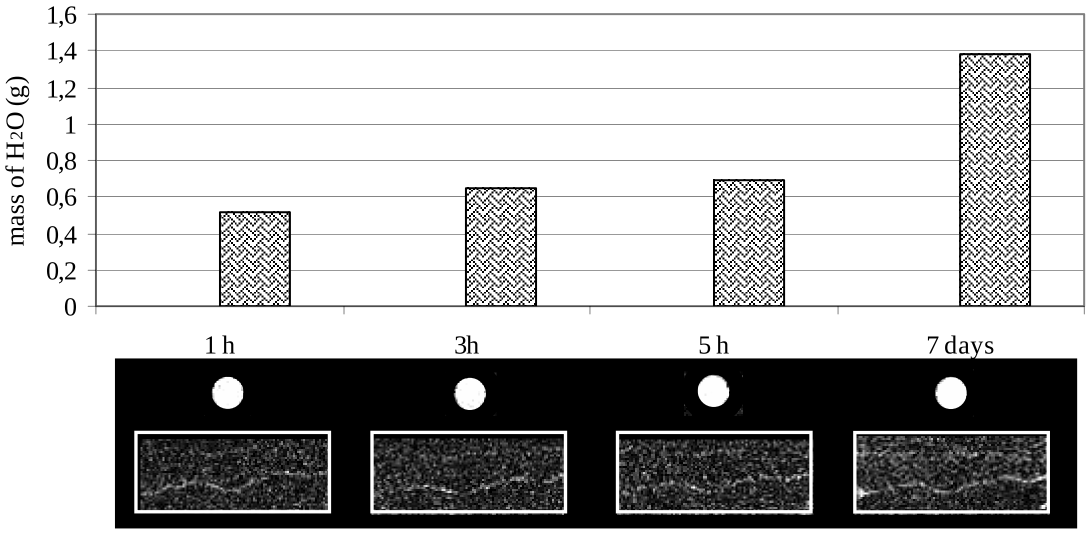

Figure 1 : MR images of a section within a sample of travertine and mass determinations of the water absorbed after different times of capillary water uptake. The lower face was placed in contact with liquid water. Brighter zones indicate higher detectable proton densities.

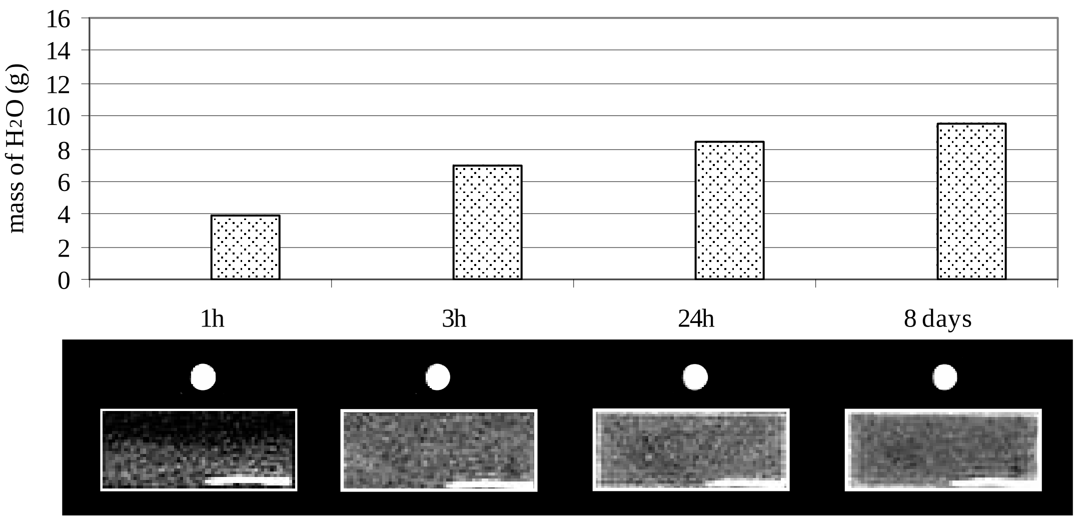

Figure 2 : MR images of a section within a sample of Lecce stone and mass determinations of the water absorbed after different times of capillary water uptake. The lower face was placed in contact with liquid water.

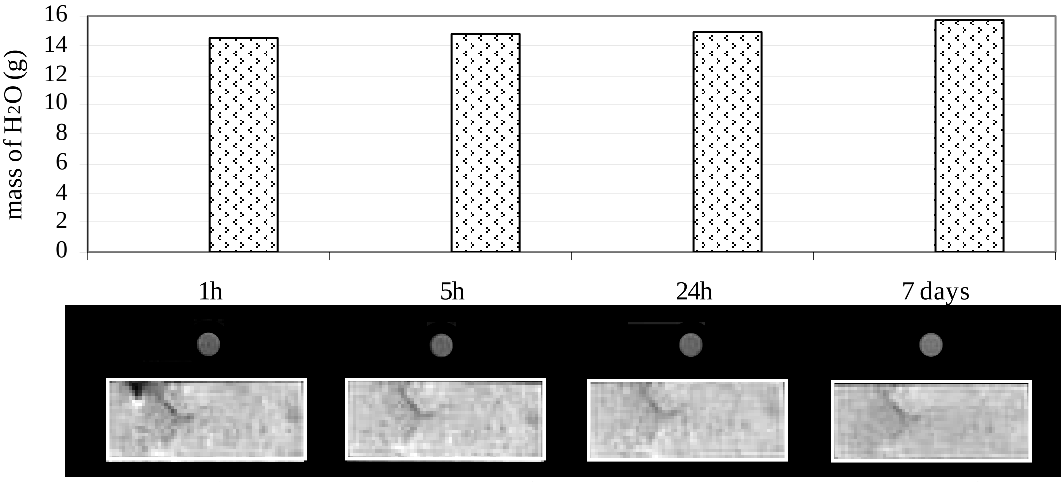

Figure 3 : MR images of a section within a sample of Matera stone and mass determinations of the water absorbed after different times of capillary water uptake. The lower face was placed in contact with liquid water.

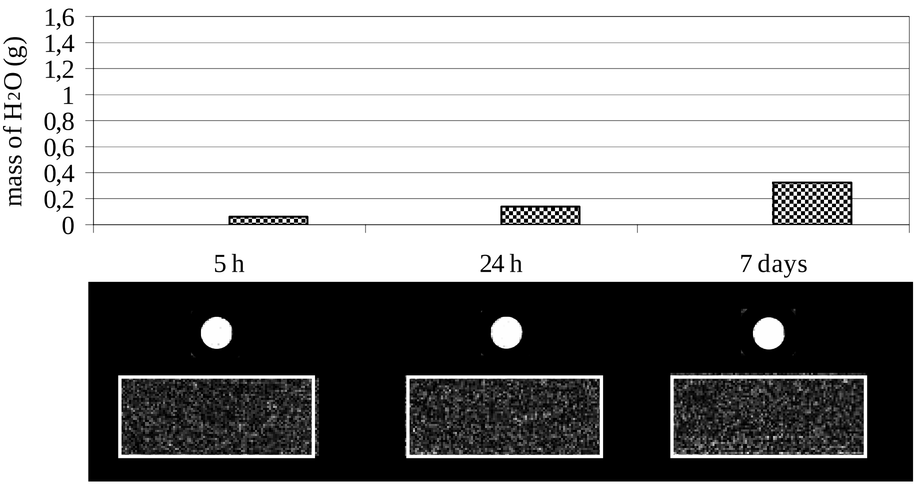

Figure 4 : MR images and mass determinations of the capillary water absorbed for a sample of travertine treated with ethyl silicate by brush (164mg/100g of stone of active product) after different times of absorption. The upper face is the treated one.

Ethyl silicate applied by brush on Lecce stone, on the contrary, has penetrated approximately 1cm, and the MR images show a dark region until 24h of water absorption (Fig. 5). After 8 days of water absorption the mass of water reaches the value obtained on average in the untreated samples, proving a uniform distribution of the product without pores filling.

A different behaviour is observed when Lecce stone is treated with a chloroform solution of PB 72 (Figs. 6, 7). The treatment by brush shows kinetics of water absorption similar to that observed in the untreated sample (Fig. 6). Only when the water uptake was carried out through the treated face did the MR images appear dark (images not reported), indicating a distribution of the polymer limited to the surface. Treatment by capillary absorption, on the contrary, shows better distribution of the PB 72 even if the penetration depth does not reach the whole height of the sample (2 cm) (Fig. 7).

The high porosity and the particular porous structure of the Matera stone, which permits the fast absorption and diffusion of water, also controls the penetration of the organic products. High penetration depth for PB 72 and ethyl silicate is reached for treatment by brush as shown in Fig. 8, and no pore blockage occurs because the water diffuses in the whole sample after long time of exposure to liquid water.

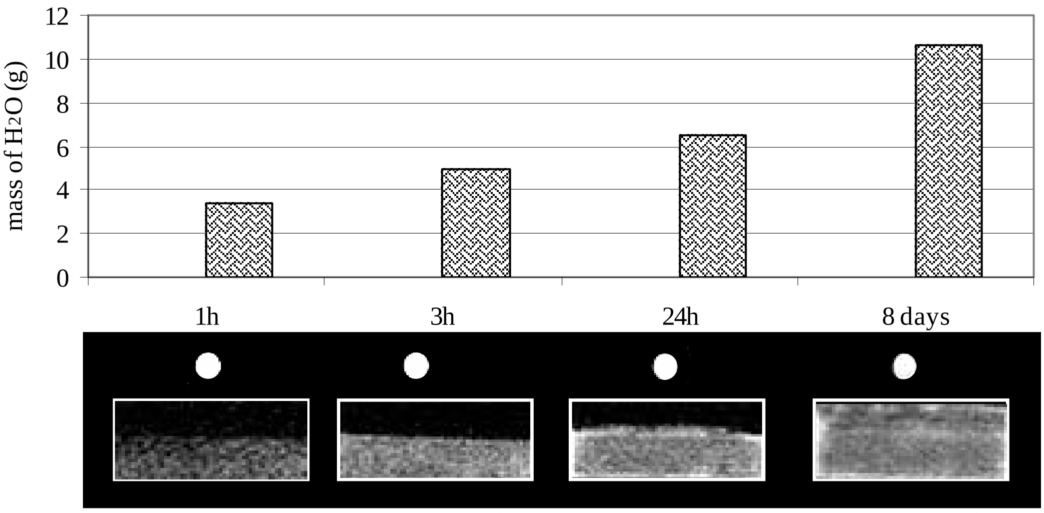

Figure 5 : MR images and mass determinations of the capillary water absorbed for a sample of Lecce stone treated with ethyl silicate by brush (814mg/100g of stone of active product) after different times of absorption. The upper face is the treated one. The lower face was placed in contact with liquid water.

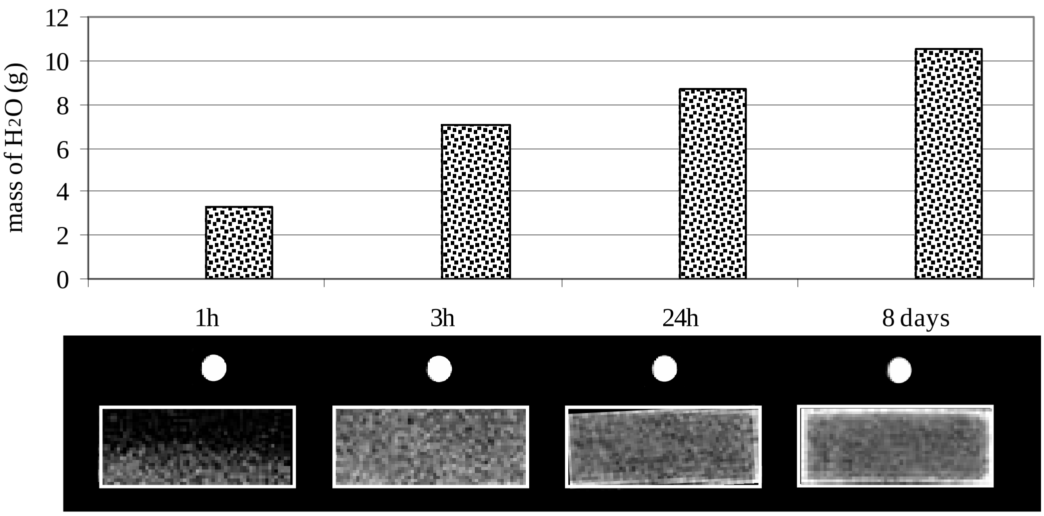

Figure 6 : MR images and mass determinations of the capillary water absorbed for a sample of Lecce stone treated with PB 72 by brush (74mg/100g of stone of active product) after different times of absorption. The upper face is the treated one.

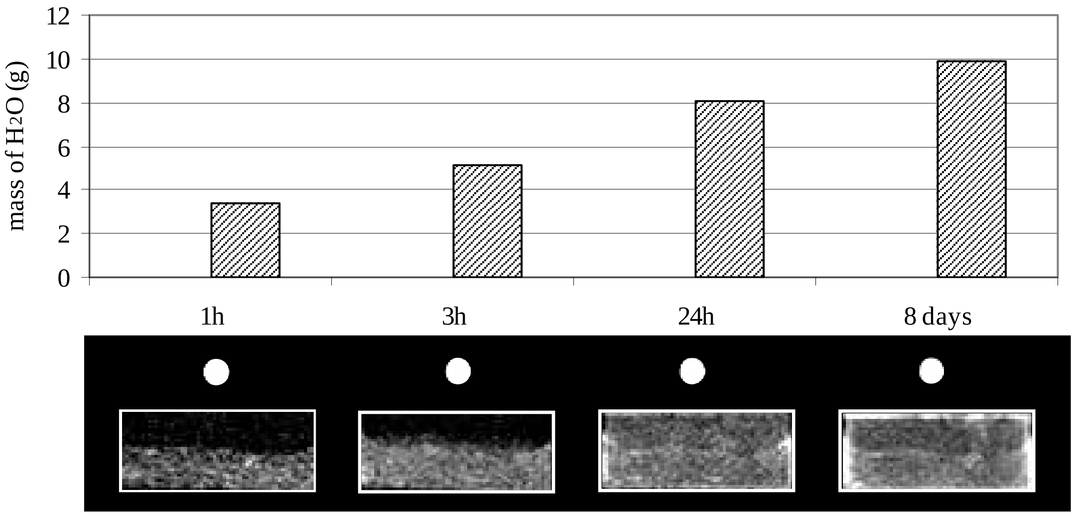

Figure 7 : MR images and mass determinations of the capillary water absorbed for a sample of Lecce stone treated with PB 72 by capillary absorption (190mg/100g of stone of active product) after different times of absorption. The upper face is the treated one.

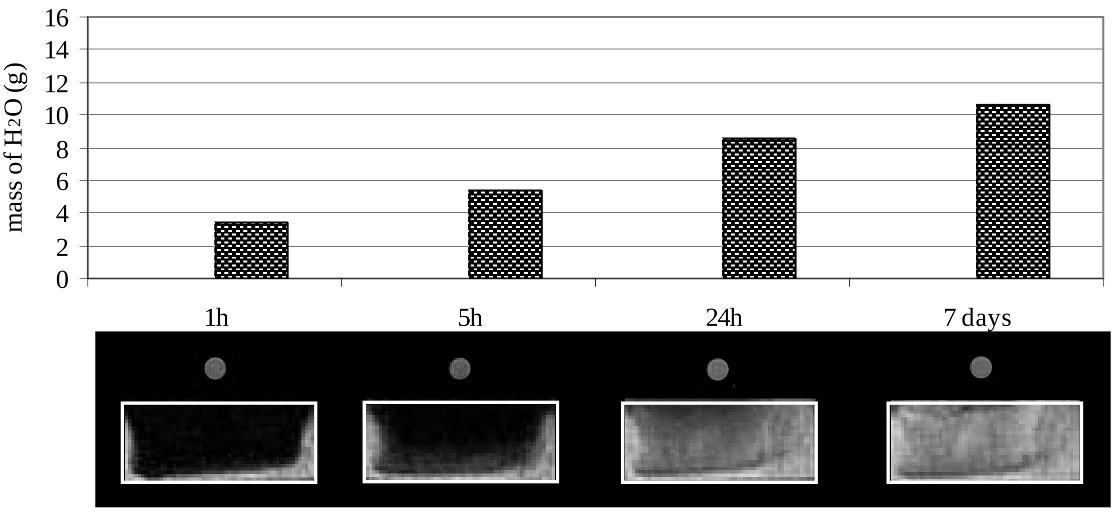

Figure 8 : MR images and mass determinations of the capillary water absorbed for a sample of Matera stone treated with PB 72 + W-OH by brush (497mg/100g of stone of PB 72 and 388mg/100g of stone of silica gel) after different times of absorption. The upper face is the treated one.

4 CONCLUSIONS

In this paper the high performance afforded by Magnetic Resonance Imaging in detecting the capillary properties of rocks and in evaluating the efficacy of the hydrophobic treatments has been confirmed.

In this work two chemical compounds have been applied to suitable stone samples and their performance evaluated. In particular there is a twofold advantage in using chemical products to protect materials which are relevant for Cultural Heritage: on one hand, these compounds inhibit the direct contact between the rock and the liquid water, which is the major deterioration agent; on the other hand they may strengthen the mechanical properties of the decayed stones. The polymers tested, applied by brush or by capillary absorption, are Paraloid B-72 (poly ethyl methacrylate-co-methyl acrylate 70/30) (PB 72) and ethyl silicate (W-OH). The stones, where the polymers have been brushed or capillary absorbed, are Lecce stone, travertine, and Matera stone. Several images acquired at different times of capillary water uptake, using an MRI tomograph, have been recorded before and after the treatments in order to evaluate their efficacy by visualizing the diffusion of liquid water. The mass of water absorbed by the rock has also been determined to quantify the water absorbed by each sample before and after the treatment.

A good penetration depth was observed in all the lithotype for the treatments carried out with small molecules (ethyl silicate). On the contrary, the application of a macromolecular product (PB 72) gives better penetration depth when highly porous stones with large pores are tested or treatment by capillary absorption is performed.

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