INVESTIGATING HYDROGEL DESALINATION OF EGYPTIAN LIMESTONE OBJECTS USING NMR-MOUSE SPECTROSCOPY

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Introduction

Soluble salts within limestone objects are a major challenge for the Cultural Heritage field. Fluctuations in humidity during storage cause salts to dissolve, migrate, and recrystallize leading to loss of structural stability of the object (Fig. 1). While full submersion into water is traditionally used, fragile objects require the use of a poultice.[1] Egyptian limestone objects in the collection of the Walters Art Museum require desalination with an agarose hydrogel poultice (Fig. 2). Prior to the desalination, the surface is secured with an organic polymer consolidant to preserve structural integrity, but the effect of this consolidant on the treatment is unknown.

Figure 1. Salt crystals causing flaking, captured by a Dino-Lite microscope.

Figure 2. 2nd-1st century BC Ptolemaic Egyptian column (ID: 22.52).

This project monitors and evaluates the efficacy of a 3% agarose hydrogel for desalination with and without a consolidant using a Profile NMR-MOUSE spectrometer (Fig. 3). This portable, non-invasive analytical technique affords in-situ depth profile and relaxometry measurements of the salt water and hydrogel, affording real-time observation of the egress of salt water from stone to gel.[2] T_2^* (spin-spin) relaxation times decrease with decreasing salinity and T_2^* rates measured over the course of the treatment allows direct observation of the salinity changes in the stone. Additionally, objects at the Walters were also analyzed for salt content.

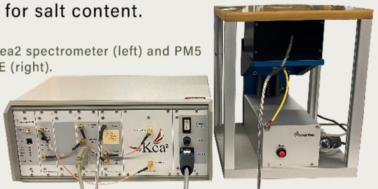

Figure 3. Kea2 spectrometer (left) and PM5 NMR-MOUSE (right).

Materials and Methods

Indiana limestone samples were dried in a vacuum oven at 130°C for 48hrs, soaked in 30% (w/v) NaCl solution for 48hrs and analyzed before and after applying a 3% agarose gel. The stone samples were consolidated with paraloid B-72, an ethyl methacrylate-methyl acrylate copolymer (Fig. 4).

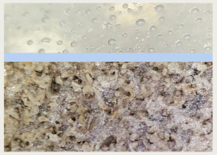

Figure 4. Layers of stone, consolidant, and gel

Desalination was monitored using a Profile PM5 NMR-MOUSE connected to a Kea2 spectrometer operating at 18.9MHz (1H). T_2^* measurements used a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence with 1024 echoes, 512 scans, and an 80µs echo time.[3] All resulting relaxation data, including spatially resolved T_2 mapping, were processed using the Inverse Laplace Transform (L&H algorithm) in Prospa V3.39.[4]

Salt analysis was performed using microchemical tests[5], Inductively Coupled Plasma-Mass spectrometry (ICP-MS), and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS).

Results and Discussion

NMR-MOUSE analysis determined that T_2^* decay time of stones soaked in 0%, 10%, 20%, and 30% NaCl water solutions were 15.3, 16.4, 17.7, and 20.5ms, respectively. For the non-consolidated stone, the T_2^* decreased from 17.7ms before treatment to 15.3ms after 5d of treatment and remained unchanged after 11d (Fig. 5). In the consolidated stone, the T_2^* decreased from 17.7ms to 16.4ms after 5d of treatment and to 15.8ms after 11d.

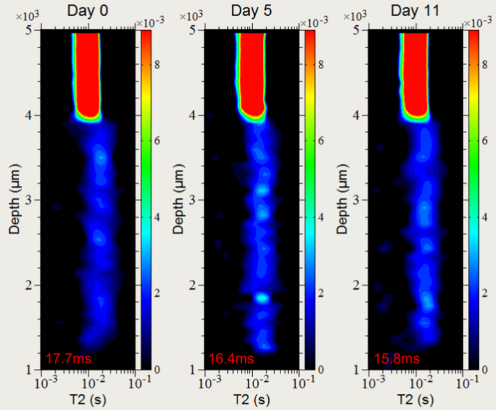

Figure 5. Spatially resolved T_2 mapping including the gel (top 1000µm) and consolidated stone (lower 3000µm) during treatment. T_2^* decay time shifts lower as treatment progresses, suggesting desalination of stone.

These data suggest that desalination is complete after 5d for the non-consolidated stones and after 11d for the consolidated stone, supporting the conclusion that consolidated stones undergo desalination at a slower rate than non-consolidated ones. Despite the slower desalination process, full desalination did occur over a reasonable treatment timeline for both.

	Concentration (ppb) in 1 mg/mL Solution				
Sample ID	Ca	K	Li	Mg	Na
Control	171,836.50	70.1	BLQ	1,578.90	382.9
22.154	122,466.90	318.8	BLQ	3,859.20	27,286.90
22.52	70,575.10	2,544.30	BLQ	5,426.20	10,570.50
22.151	113,724.80	490	BLQ	3,844.70	12,093.60

Figure 6. Results from the PerkinElmer NexION 300D mass spectrometer with ICP ionization. Samples: Indiana limestone (control) and samples from the Walters Art Museum (Object ID: 22.151, 22.52, 22.154).

Salt characterization was performed on samples from three objects in the Walters' collection. Microchemical salt tests were consistent with the presence of PO_4^{3-}, SO_4^{2-}, and Cl^- and an absence of NO_3^- in all three samples. ICP-MS analysis determined the concentration of Ca^{2+}, K^+, Li^+, Mg^{2+}, and Na^+ present in each sample (Fig. 6). SEM/EDS analysis suggests the presence of NaCl and some common limestone impurities in each.

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Conclusion

This study examined the efficacy of using agarose gel poultices for desalinating fragile limestone objects. While desalination occurs at a slower rate in consolidated stones, treatment is still viable. Additionally, salt analysis performed may help to develop object environment conditions for long-term storage, as different salts recrystallize and cause damage at different humidity levels. Future research can be conducted to examine how consolidation and treatment affect the appearance of limestone objects.

References

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