Can the mineral constituting our teeth and bones help us preserve our monuments? The HAP4MARBLE project

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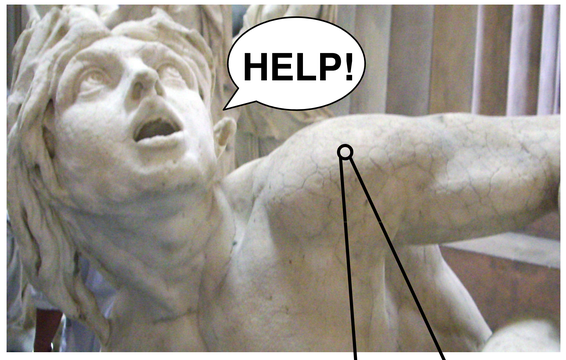
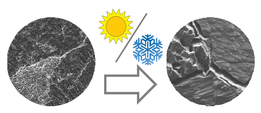
BACKGROUND



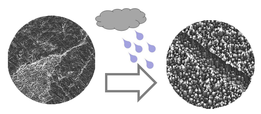
Many sculptures & monuments are made of **marble**, which is composed of calcite grains

When exposed outdoor marble **deteriorates** because:

- **Temperature variations** cause the opening of cracks between calcite grains, so that grains detach and fall



- **Rain** causes the dissolution of calcite grains, so that the marble carved surface is lost



The **products currently available** are not effective and/or durable in preserving marble against these deterioration causes

We have recently started investigating the possible use of **hydroxyapatite (HAP)**, the mineral constituting our teeth and bones, to preserve marble monuments [1]

HAP can be formed directly inside marble and over marble surface in mild conditions

RESEARCH AIMS

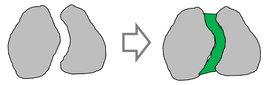
1 *Accelerated ageing*

How can we produce **artificially aged** (cracked) samples to test HAP?

2 *Reaction parameters*

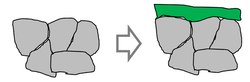
What are the best **treatment conditions** to favor HAP formation?

3 *Consolidation*



Is HAP effective in **restoring the strength** of weathered marble?

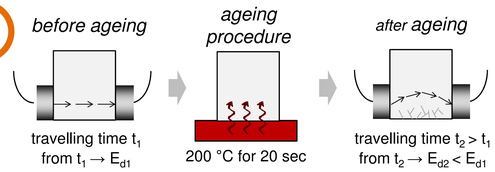
4 *Protection*



Is HAP effective in **preventing the dissolution** of marble surface in rain?

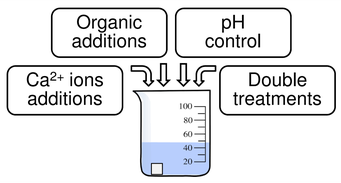
EXPERIMENTAL PROCEDURE

1



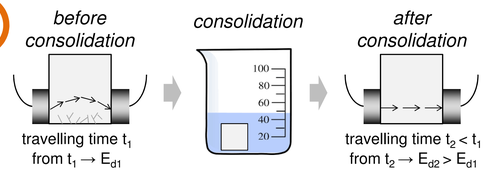
Ageing was produced by heating samples over a **hot plate** for a short time and the damage was assessed by measuring the **modulus E_d** (related to strength)

2



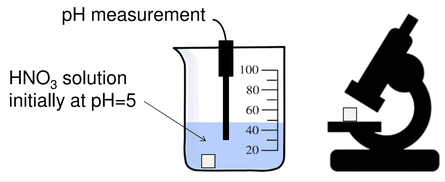
The influence of several **treatment parameters** (organic additions [2], Ca^{2+} ions addition [3], pH control and double treatments) was investigated

3



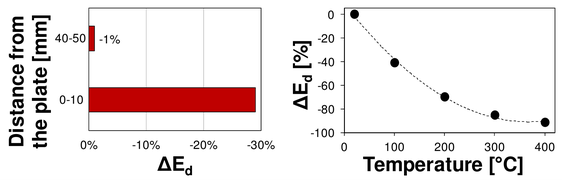
The increase in marble cohesion after consolidation was assessed by measuring the **modulus E_d** before and after the treatment on exactly the same sample

4

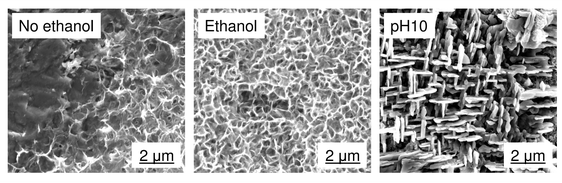


The resistance to dissolution was assessed by measuring the **increase in pH** *vs* time of an aqueous solution of HNO_3 initially at pH=5 (simulating slightly acid rain)

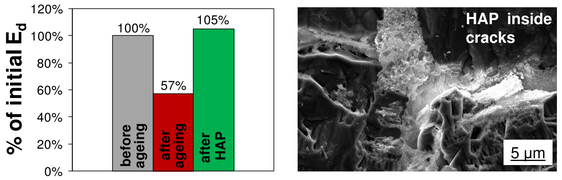
RESULTS AND DISCUSSION



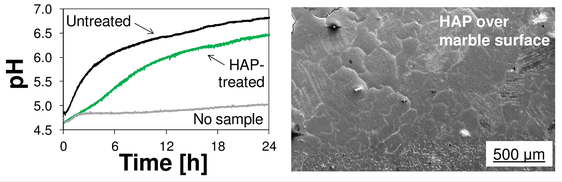
Heating at 200 °C for 20 sec caused **near-surface damage** similar to that of naturally weathered marble (higher damage at higher temperature)



The coverage of marble surface and the new phases morphology were found to be highly influenced by **ethanol addition** and **pH increase**



HAP was able to **fully restore** the modulus of marble preliminarily damaged at 100 °C, thanks to HAP formation inside cracks



HAP was able to significantly **reduce the dissolution** of marble (even if the HAP film was cracked at the end of the acid attack test)

CONCLUSIONS AND FUTURE WORK

The **addition of ethanol** was effective in promoting HAP formation, even if it has competitive effects (adsorption on marble surface and weakening of Ca^{2+} ions hydration shell)

Investigation of HAP for tackling further marble decay processes, such as **bowing** of thin slabs used as gravestones and cladding elements and **soiling** owing to atmospheric particles

ACKNOWLEDGEMENTS

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REFERENCES

[1] Sassoni E., Naidu S., Scherer G.W., *The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones*, J Cult Herit 12 (2011) 346-355
[2] Graziani G., Sassoni E., Franzoni E., Scherer G.W., *Hydroxyapatite coatings for marble protection: Optimization of calcite covering and acid resistance*, Appl Surf Sci, 368 (2016) 241-257 [3] Naidu S. & Scherer G.W., *Nucleation, growth and evolution of calcium phosphate films on calcite*, J Colloidal Interf Sci 435 (2014) 128-137