Conservation of sugaring marble by hydroxyapatite:
some recent developments on producing and treating decayed samples

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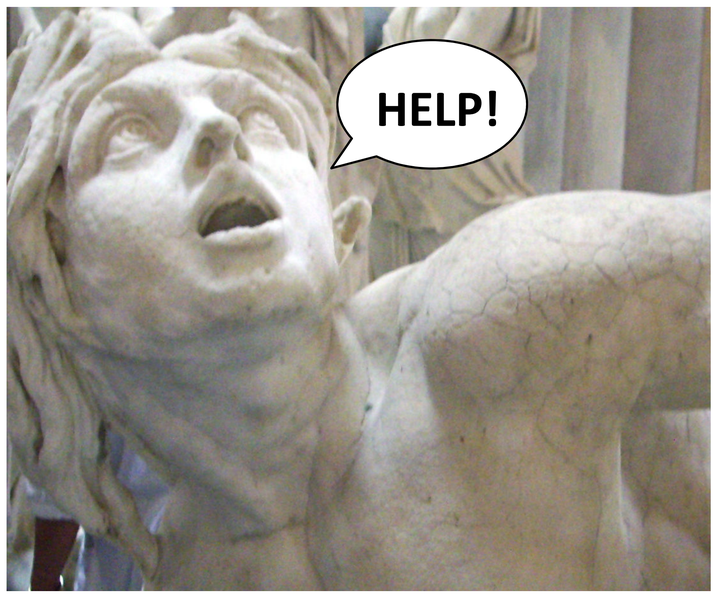
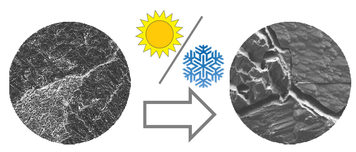
BACKGROUND

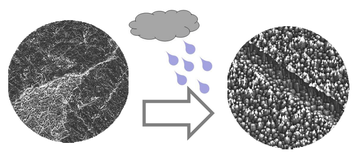


Architectural decorations and sculptures made of marble, when they are exposed outdoor, **deteriorate** because:

• **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

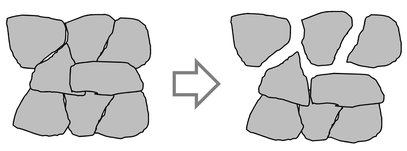
In 2011, we proposed the use of **hydroxyapatite (HAP)** to preserve carbonate stones [1]

HAP can be formed directly inside marble and over marble surface, from the reaction between **calcite** and an aqueous solution of diammonium hydrogen phosphate (**DAP**) in mild conditions

RESEARCH AIMS

Accelerated ageing

1



To study the consolidating efficacy of the HAP treatment, artificially aged samples with characteristics similar to naturally sugaring marble (i.e. **micro-cracks more diffused near the surface**) are needed

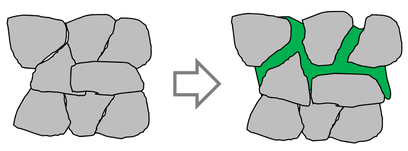
Treatment parameters

2

The treatment parameters need to be optimized to **reduce the porosity** of the HAP layer, increase the surface coverage and prevent the formation of soluble calcium phosphate phases

Consolidation

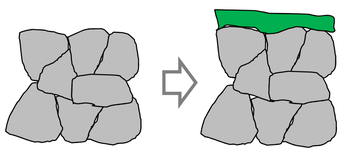
3



The ability of the HAP treatment to re-establish cohesion between calcite grains and **restore the strength** of weathered marble, without causing over-consolidation, needs to be investigated

Protection

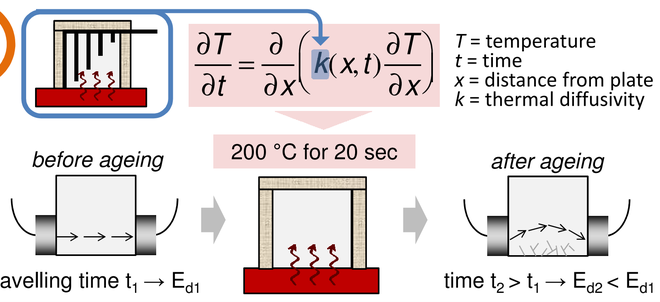
4



The ability of the HAP treatment to **prevent the dissolution** of marble surface in rain, by formation of a dense coating with low solubility, needs to be investigated

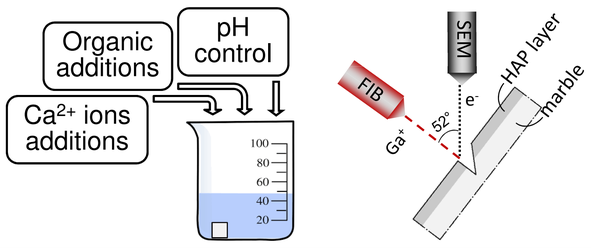
MATERIALS AND METHODS

1



Ageing was produced by heating samples over a **hot plate**, the temperature and time of heating being calculated by a **theoretical model**. Damage was assessed by measuring the **modulus E_d**

2

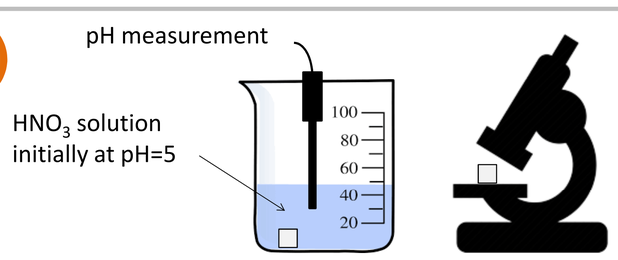


The influence of several **treatment parameters** (ethanol addition, pH control, double treatments [2]) was investigated and the effects evaluated by SEM-FIB

3

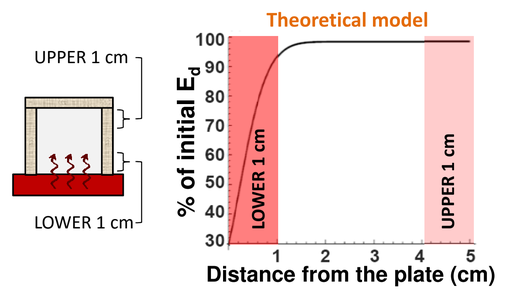
The increase in marble cohesion after consolidation was assessed by measuring the increase in **modulus E_d** and observing the new phosphate phases by **ESEM**

4

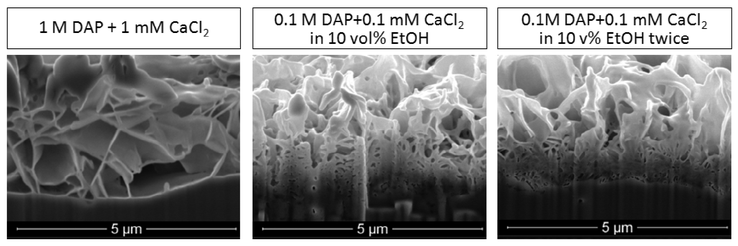


The resistance to dissolution was assessed by measuring the **increase in pH *vs* time** of an aqueous solution of HNO_3 initially at pH=5 (simulating slightly acid rain)

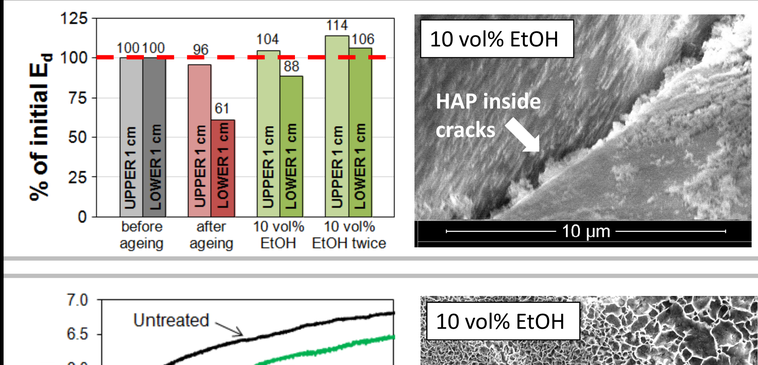
RESULTS AND DISCUSSION



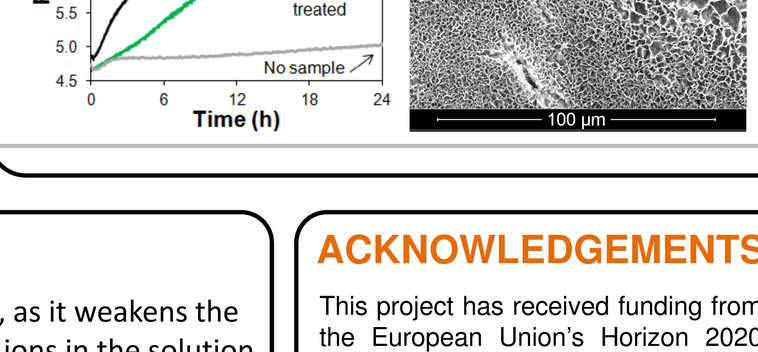
Heating at 200 °C for 20 sec was **predicted** to cause an average **ΔE_d = -35%** in the first 1 cm from the surface, leaving the rest undamaged. **Experimental results confirmed** the prediction



Ethanol addition favors marble surface coverage and helps **reduce the porosity** of the HAP layer, as it weakens the hydration shell of the phosphate ions in solution



Double application of the HAP treatment with 10 vol% ethanol was able to **fully restore the E_d**, thanks to HAP formation inside cracks formed by artificial ageing



The HAP coating was able to **reduce marble dissolution**, even if cracks appeared after the test. The orientation of the underlying calcite grains influences the film durability

CONCLUSIONS AND FUTURE WORK

The developed model allows to produce samples with a **desired level of damage**.

The **addition of ethanol** is effective in promoting HAP formation and reducing the film porosity, thus allowing to achieve a good consolidating and protecting ability

Ethanol has a **competitive effect**, as it weakens the hydration shell of the phosphate ions in the solution but it is adsorbed on calcite surface.

Future research will be aimed at identifying by **NMR** possible **alternative solvents** that may weaken the hydration shell without being adsorbed on calcite

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