

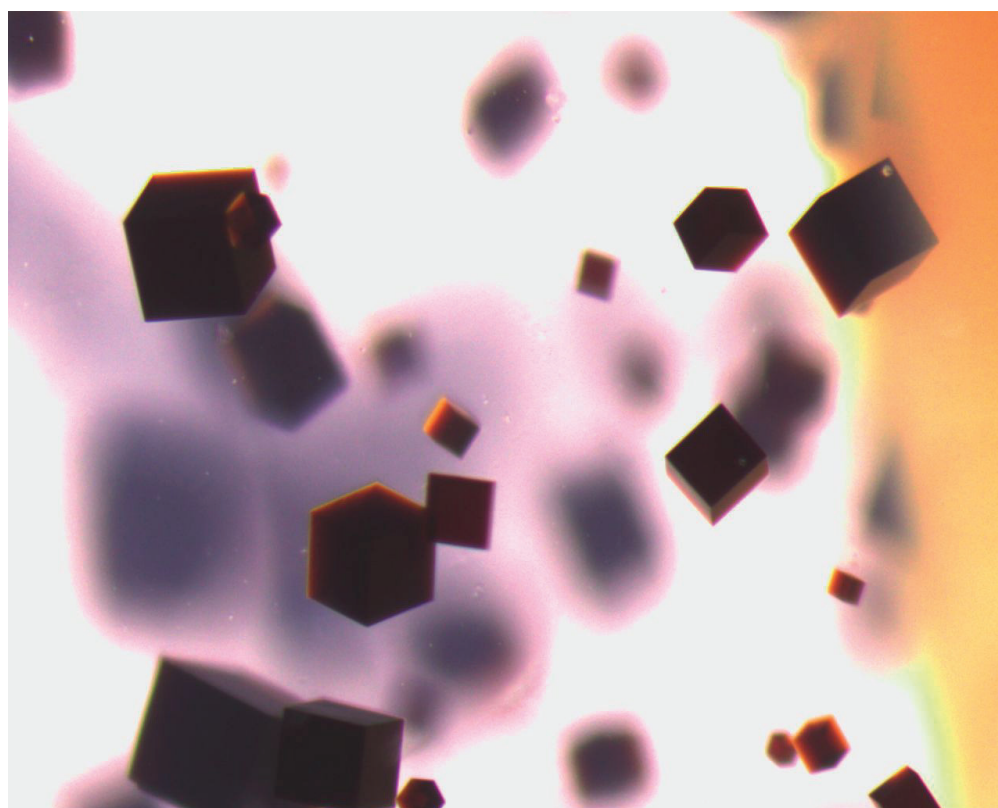


Milano, 20-21 November 2017

Italian Crystal Growth 2017

materials and methods in crystal growth

Book of Abstracts



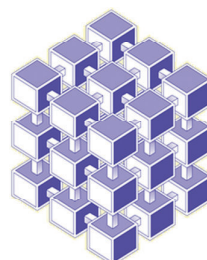
UNIVERSITÀ DEGLI STUDI
DI MILANO



Milano (Italy), November 20 – 21, 2017



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Molecular
Dimensions



**Banca Popolare
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ASSOCIAZIONE ITALIANA DI CRISTALLOGRAFIA
(Crystal Growth Section of Italian Association of Crystallography)



Italian Crystal Growth 2017

materials and methods in crystal growth

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This year we celebrate the 50th anniversary
of the Italian Association of Crystallography

University of Milano-Bicocca
Milano (Italy), November 20 – 21, 2017

T1 – O4

Crystallization of calcium phosphates on carbonatic substrates after ammonium phosphate consolidating treatments

Elena Possenti^{1,2}, *Chiara Colombo*¹, *Claudia Conti*¹, *Giacomo Diego Gatta*², *Marco Merlini*²,
*Marco Realini*¹

1. Institute for the Conservation and Valorization of Cultural Heritage (ICVBC-CNR), Via R. Cozzi 53, 20125, Milan (Italy)
2. Earth Science Department, University of Milan, Via Botticelli 23, 20133, Milan (Italy)

elena.possenti@unimi.it

Diammonium hydrogenphosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$) is a promising candidate for consolidating treatment for carbonatic substrates of decayed ornamental stones. The treatment gives rise to the formation of calcium phosphates through a mild reaction of dissolution and re-crystallization¹, which takes place between hydrogen phosphate groups of the reagent and calcium ions of calcite of the substrate. Calcium phosphates nucleate on calcite boundaries with a pseudomorphic replacement reaction², and grow on pre-reacted profiles of calcite grains. In recent investigations³, it was observed that the reaction of DAP solutions with calcite induces the formation of calcium phosphates in a multiphase assemblage. The formation of specific crystalline phases and their arrangements on the stone substrate governs the performance of inorganic-mineral consolidating treatments. It follows that the survey of the mechanism that rules the formation of calcium phosphates on calcite is crucial in conservation field but their investigation, especially when in mixtures, is an analytical challenge.

In this work, we present a new multi-analytical approach in order to characterize the newly-formed crystalline phases and their distribution on calcite of the substrate.

Our experimental results show that the DAP reaction with calcite forms stable hydroxyapatite (HAP, $(\text{Ca}_5(\text{PO}_4)_3\text{OH})$) and metastable brushite (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and octacalcium phosphate (OCP, $\text{Ca}_8(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$) as well as amorphous compounds (*e.g.*, ACP, amorphous calcium phosphate, $\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$, with $n = 3-4.5$). The formation of specific phases and their morphology seems to be directly influenced by the duration of the treatment, by the microstructure of the stone matrix and by the DAP molarity. Moreover, the pH variation during the reaction affects the growth of HAP and OCP, inducing the formation of inter-layered sub-micrometric individuals.

This research supplies a new analytical approach for the characterization of calcium phosphates multi-phase mixture and it paves the way to a critical evaluation of DAP treatments applied on Cultural Heritage surfaces.

References

¹ Possenti *et al.*, *Microchem. J.* **2016**, 127, 79

² Kasiopas *et al.*, *Mineral. Mag.* **2008**, 72, 77

³ (a) Matteini *et al.*, *Int. J. Archit. Herit. Conserv. Anal. Restor.* **2011**, 5, 717; (b) Matteini *et al.*, *Ammonium phosphates to consolidate carbonatic stone materials: an inorganic-mineral treatment greatly promising*, **2013**, Proceedings of the Built Heritage Monitoring Conservation Management