

Methods of Consolidation and Protection of Pentelic Marble

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Daniela Matetić Poljak
Katja Marasović



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CONTENT

PRESENTATION	15
NECROLOGY: NORMAN HERZ (1923-2013) by Susan Kane	17
1. APPLICATIONS TO SPECIFIC ARCHEOLOGICAL QUESTIONS – USE OF MARBLE	
Hermaphrodites and Sleeping or Reclining Maenads: Production Centres and Quarry Marks <i>Patrizio Pensabene</i>	25
First Remarks about the Pavement of the Newly Discovered Mithraeum of the Colored Marbles at Ostia and New Investigations on Roman and Late Roman White and Colored Marbles from Insula IV, IX <i>Massimiliano David, Stefano Succi and Marcello Turci</i>	33
Alabaster. Quarrying and Trade in the Roman World: Evidence from Pompeii and Herculaneum <i>Simon J. Barker and Simona Perna</i>	45
Recent Work on the Stone at the Villa Arianna and the Villa San Marco (Castellammare di Stabia) and Their Context within the Vesuvian Area <i>Simon J. Barker and J. Clayton Fant</i>	65
Marble Wall Decorations from the Imperial Mausoleum (4 th C.) and the Basilica of San Lorenzo (5 th C.) in Milan: an Update on Colored Marbles in Late Antique Milan <i>Elisabetta Neri, Roberto Bugini and Silvia Gazzoli</i>	79
Sarcophagus Lids Sawn from their Chests <i>Dorothy H. Abramitis and John J. Herrmann</i>	89
The Re-Use of Monolithic Columns in the Invention and Persistence of Roman Architecture <i>Peter D. De Staebler</i>	95
The Trade in Small-Size Statues in the Roman Mediterranean: a Case Study from Alexandria <i>Patrizio Pensabene and Eleonora Gasparini</i>	101
The Marble Dedication of Komon, Son of Asklepiades, from Egypt: Material, Provenance, and Reinforcement of Meaning <i>Patricia A. Butz</i>	109
Multiple Reuse of Imported Marble Pedestals at Caesarea Maritima in Israel <i>Barbara Burrell</i>	117
Iasos and Iasian Marble between the Late Antique and Early Byzantine Eras <i>Diego Peirano</i>	123

Thassos, Known Inscriptions with New Data <i>Tony Kozelj and Manuela Wurch-Kozelj</i>	131
The Value of Marble in Roman <i>Hispalis</i> : Contextual, Typological and Lithological Analysis of an Assemblage of Large Architectural Elements Recovered at N° 17 Goyeneta Street (Seville, Spain) <i>Ruth Taylor, Oliva Rodríguez, Esther Ontiveros, María Luisa Loza, José Beltrán and Araceli Rodríguez</i>	143
<i>Giallo Antico</i> in Context. Distribution, Use and Commercial Actors According to New Stratigraphic Data from the Western Mediterranean (2 nd C. Bc – Late 1 st C. Ad) <i>Stefan Ardeleanu</i>	155
<i>Amethystus</i> : Ancient Properties and Iconographic Selection <i>Luigi Pedroni</i>	167
2. PROVENANCE IDENTIFICATION I: (MARBLE)	
Unraveling the Carrara – Göktepe Entanglement <i>Walter Prochaska, Donato Attanasio and Matthias Bruno</i>	175
The Marble of Roman Imperial Portraits <i>Donato Attanasio, Matthias Bruno, Walter Prochaska and Ali Bahadır Yavuz</i>	185
Tracing Alabaster (Gypsum or Anhydrite) Artwork Using Trace Element Analysis and a Multi-Isotope Approach (Sr, S, O) <i>Lise Leroux, Wolfram Kloppmann, Philippe Bromblet, Catherine Guerrot, Anthony H. Cooper, Pierre-Yves Le Pogam, Dominique Vingtain and Noel Worley</i>	195
Roman Monolithic Fountains and Thasian Marble <i>Annewies van den Hoek, Donato Attanasio and John J. Herrmann</i>	207
Archaeometric Analysis of the Alabaster Thresholds of Villa A, Oplontis (Torre Annunziata, Italy) and New Sr and Pb Isotopic Data for <i>Alabastro Ghiaccione del Circeo</i> <i>Simon J. Barker, Simona Perna, J. Clayton Fant, Lorenzo Lazzarini and Igor M. Villa</i>	215
Roman Villas of Lake Garda and the Occurrence of Coloured Marbles in the Western Part of “Regio X Venetia et Histria” (Northern Italy) <i>Roberto Bugini, Luisa Folli and Elisabetta Roffia</i>	231
Calcitic Marble from Thasos in the North Adriatic Basin: Ravenna, Aquileia, and Milan <i>John J. Herrmann, Robert H. Tykot and Annewies van den Hoek</i>	239
Characterisation of White Marble Objects from the Temple of Apollo and the House of Augustus (Palatine Hill, Rome) <i>Francesca Giustini, Mauro Brilli, Enrico Gallochio and Patrizio Pensabene</i>	247
Study and Archeometric Analysis of the Marble Elements Found in the Roman Theater at Aeclanum (Mirabella Eclano, Avellino - Italy) <i>Antonio Mesisca, Lorenzo Lazzarini, Stefano Cancelliere and Monica Salvadori</i>	255

Two Imperial Monuments in Puteoli: Use of Proconnesian Marble in the Domitianic and Trajanic Periods in Campania <i>Irene Bald Romano, Hans Rupprecht Goette, Donato Attanasio and Walter Prochaska</i>	267
Coloured Marbles in the Neapolitan Pavements (16 th And 17 th Centuries): the Church of <i>Santi Severino e Sossio</i> <i>Roberto Bugini, Luisa Folli and Martino Solito</i>	275
Roman and Early Byzantine Sarcophagi of Calcitic Marble from Thasos in Italy: Ostia and Siracusa <i>Donato Attanasio, John J. Herrmann, Robert H. Tykot and Annewies van den Hoek</i>	281
Revisiting the Origin and Destination of the Late Antique Marzamemi 'Church Wreck' Cargo <i>Justin Leidwanger, Scott H. Pike and Andrew Donnelly</i>	291
The Marbles of the Sculptures of Felix Romuliana in Serbia <i>Walter Prochaska and Maja Živić</i>	301
Calcitic Marble from Thasos and Proconnesos in Nea Anchialos (Thessaly) and Thessaloniki (Macedonia) <i>Vincent Barbin, John J. Herrmann, Aristotle Mentzos and Annewies van den Hoek</i>	311
Architectural Decoration of the Imperial Agora's Porticoes at Iasos <i>Fulvia Bianchi, Donato Attanasio and Walter Prochaska</i>	321
The Winged Victory of Samothrace - New Data on the Different Marbles Used for the Monument from the Sanctuary of the Great Gods <i>Annie Blanc, Philippe Blanc and Ludovic Laugier</i>	331
Polychrome Marbles from the Theatre of the Sanctuary of Apollo Pythios in Gortyna (Crete) <i>Jacopo Bonetto, Nicolò Mareso and Michele Bueno</i>	337
Paul the Silentiary, Hagia Sophia, Onyx, Lydia, and Breccia Corallina <i>John J. Herrmann and Annewies van den Hoek</i>	345
Incrustations from Colonia Ulpia Traiana (Near Modern Xanten, Germany) <i>Vilma Ruppinić and Ulrich Schüssler</i>	351
Stone Objects from Vindobona (Austria) – Petrological Characterization and Provenance of Local Stone in a Historico-Economical Setting <i>Andreas Rohatsch, Michaela Kronberger, Sophie Insulander, Martin Mosser and Barbara Hodits</i>	363
Marbles Discovered on the Site of the Forum of Vaison-la-Romaine (Vaucluse, France): Preliminary Results <i>Elsa Roux, Jean-Marc Mignon, Philippe Blanc and Annie Blanc</i>	373
Updated Characterisation of White Saint-Béat Marble. Discrimination Parameters from Classical Marbles <i>Hernando Royo Plumed, Pilar Lapeunte, José Antonio Cuchí, Mauro Brillì and Marie-Claire Savin</i>	379

Grey and Greyish Banded Marbles from the Estremoz Anticline in Lusitania <i>Pilar Lapuente, Trinidad Nogales-Basarrate, Hernando Royo Plumed, Mauro Brilli and Marie-Claire Savin</i>	391
New Data on Spanish Marbles: the Case of <i>Gallaecia</i> (NW Spain) <i>Anna Gutiérrez García-M., Hernando Royo Plumed and Silvia González Soutelo</i>	401
A New Roman Imperial Relief Said to Be from Southern Spain: Problems of Style, Iconography, and Marble Type in Determining Provenance <i>John Pollini, Pilar Lapuente, Trinidad Nogales-Basarrate and Jerry Podany</i>	413
Reuse of the <i>Marmora</i> from the Late Roman Palatial Building at Carranque (Toledo, Spain) in the Visigothic Necropolis <i>Virginia García-Entero, Anna Gutiérrez García-M. and Sergio Vidal Álvarez</i>	427
Imperial Porphyry in Roman Britain <i>David F. Williams</i>	435
Recycling of Marble: Apollonia/Sozousa/Arsuf (Israel) as a Case Study <i>Moshe Fischer, Dimitris Tambakopoulos and Yannis Maniatis</i>	443
Thasian Connections Overseas: Sculpture in the Cyrene Museum (Libya) Made of Dolomitic Marble from Thasos <i>John J. Herrmann and Donato Attanasio</i>	457
Marble on Rome's Southwestern Frontier: Thamugadi and Lambaesis <i>Robert H. Tykot, Ouahiba Bouzidi, John J. Herrmann and Annewies van den Hoek</i>	467
Marble and Sculpture at Lepcis Magna (Tripolitania, Libya): a Preliminary Study Concerning Origin and Workshops <i>Luisa Musso, Laura Buccino, Matthias Bruno, Donato Attanasio and Walter Prochaska</i>	481
The Pentelic Marble in the Carnegie Museum of Art Hall of Sculpture, Pittsburgh, Pennsylvania <i>Albert D. Kollar</i>	491
Analysis of Classical Marble Sculptures in the Michael C. Carlos Museum, Emory University, Atlanta <i>Robert H. Tykot, John J. Herrmann, Renée Stein, Jasper Gaunt, Susan Blevins and Anne R. Skinner</i>	501
3. PROVENANCE IDENTIFICATION II: (OTHER STONES)	
Aphrodisias and the Regional Marble Trade. The <i>Scaenae Frons</i> of the Theatre at Nysa <i>Natalia Toma</i>	513
The Stones of Felix Romuliana (Gamzigrad, Serbia) <i>Bojan Djurić, Divna Jovanović, Stefan Pop Lazić and Walter Prochaska</i>	523
Aspects of Characterisation of Stone Monuments from Southern Pannonia <i>Branka Migotti</i>	537

The Budakalász Travertine Production <i>Bojan Djurić, Sándor Kele and Igor Rižnar</i>	545
Stone Monuments from Carnuntum and Surrounding Areas (Austria) – Petrological Characterization and Quarry Location in a Historical Context <i>Gabrielle Kremer, Isabella Kitz, Beatrix Moshhammer, Maria Heinrich and Erich Draganits</i>	557
Espejón Limestone and Conglomerate (Soria, Spain): Archaeometric Characterization, Quarrying and Use in Roman Times <i>Virginia García-Entero, Anna Gutiérrez García-M, Sergio Vidal Álvarez, María J. Peréx Agorreta and Eva Zarco Martínez</i>	567
The Use of Alcover Stone in Roman Times (<i>Tarraco, Hispania Citerior</i>). Contributions to the <i>Officina Lapidaria Tarraconensis</i> <i>Diana Gorostidi Pi, Jordi López Vilar and Anna Gutiérrez García-M.</i>	577
4. ADVANCES IN PROVENANCE TECHNIQUES, METHODOLOGIES AND DATABASES	
Grainautline – a Supervised Grain Boundary Extraction Tool Supported by Image Processing and Pattern Recognition <i>Kristóf Csorba, Lilla Barancsuk, Balázs Székely and Judit Zöldföldi</i>	587
A Database and GIS Project about Quarrying, Circulation and Use of Stone During the Roman Age in <i>Regio X - Venetia et Histria</i> . The Case Study of the Euganean Trachyte <i>Caterine Previato and Arturo Zara</i>	597
5. QUARRIES AND GEOLOGY	
The Distribution of Troad Granite Columns as Evidence for Reconstructing the Management of Their Production <i>Patrizio Pensabene, Javier Á. Domingo and Isabel Rodà</i>	613
Ancient Quarries and Stonemasonry in Northern Choria Considiana <i>Hale Güney</i>	621
Polychromy in Larisaeon Quarries and its Relation to Architectural Conception <i>Gizem Mater and Ertunç Denктаş</i>	633
Euromos of Caria: the Origin of an Hitherto Unknown Grey Veined Stepped Marble of Roman Antiquity <i>Matthias Bruno, Donato Attanasio, Walter Prochaska and Ali Bahadır Yavuz</i>	639
Unknown Painted Quarry Inscriptions from Bacakale at <i>Docimium</i> (Turkey) <i>Matthias Bruno</i>	651
The Green Schist Marble Stone of Jebel El Hairech (North West of Tunisia): a Multi-Analytical Approach and its Uses in Antiquity <i>Ameur Younès, Mohamed Gaied and Wissem Gallala</i>	659
Building Materials and the Ancient Quarries at <i>Thamugadi</i> (East of Algeria), Case Study: Sandstone and Limestone <i>Younès Rezkallah and Ramdane Marmi</i>	673

The Local Quarries of the Ancient Roman City of <i>Valeria</i> (Cuenca, Spain) <i>Javier Atienza Fuente</i>	683
The Stone and Ancient Quarries of Montjuïc Mountain (Barcelona, Spain) <i>Aureli Álvarez</i>	693
<i>Notae Lapidinarum</i> : Preliminary Considerations about the Quarry Marks from the Provincial Forum of <i>Tarraco</i> <i>Maria Serena Vinci</i>	699
The Different Steps of the Rough-Hewing on a Monumental Sculpture at the Greek Archaic Period: the Unfinished Kouros of Thasos <i>Danièle Braunstein</i>	711
A Review of Copying Techniques in Greco-Roman Sculpture <i>Séverine Moureaud</i>	717
Labour Forces at Imperial Quarries <i>Ben Russell</i>	733
Social Position of Craftsmen inside the Stone and Marble Processing Trades in the Light of Diocletian's Edict on Prices <i>Krešimir Bosnić and Branko Matulić</i>	741
6. STONE PROPERTIES, WEATHERING EFFECTS AND RESTORATION, AS RELATED TO DIAGNOSIS PROBLEMS, MATCHING OF STONE FRAGMENTS AND AUTHENTICITY	
Methods of Consolidation and Protection of Pentelic Marble <i>Maria Apostolopoulou, Elissavet Drakopoulou, Maria Karoglou and Asterios Bakolas</i>	749
7. PIGMENTS AND PAINTINGS ON MARBLE	
Painting and Sculpture Conservation in Two Gallo-Roman Temples in Picardy (France): Champlieu and Pont-Sainte-Maxence <i>Véronique Brunet-Gaston and Christophe Gaston</i>	763
The Use of Colour on Roman Marble Sarcophagi <i>Eliana Siotto</i>	773
New Evidence for Ancient Gilding and Historic Restorations on a Portrait of Antinous in the San Antonio Museum of Art <i>Jessica Powers, Mark Abbe, Michelle Bushey and Scott H. Pike</i>	783
Schists and Pigments from Ancient Swat (Khyber Pukhtunkhwa, Pakistan) <i>Francesco Mariottini, Gianluca Vignaroli, Maurizio Mariottini and Mauro Roma</i>	793
8. SPECIAL THEME SESSION: „THE USE OF MARBLE AND LIMESTONE IN THE ADRIATIC BASIN IN ANTIQUITY”	
Marble Sarcophagi of Roman Dalmatia Material – Provenance – Workmanship <i>Guntram Koch</i>	809

Funerary Monuments and Quarry Management in Middle Dalmatia <i>Nenad Cambi</i>	827
Marble Revetments of Diocletian's Palace <i>Katja Marasović and Vinka Marinković</i>	839
The Use of Limestones as Construction Materials for the Mosaics of Diocletian's Palace <i>Branko Matulić, Domagoj Mudronja and Krešimir Bosnić</i>	855
Restoration of the Peristyle of Diocletian's Palace in Split <i>Goran Nikšić</i>	863
Marble Slabs Used at the Archaeological Site of Sorna near Poreč Istria – Croatia <i>Đeni Gobić-Bravar</i>	871
Ancient Marbles from the Villa in Verige Bay, Brijuni Island, Croatia <i>Mira Pavletić and Đeni Gobić-Bravar</i>	879
Notes on Early Christian Ambos and Altars in the Light of some Fragments from the Islands of Pag and Rab <i>Mirja Jarak</i>	887
The Marbles in the Chapel of the Blessed John of Trogir in the Cathedral of St. Lawrence at Trogir <i>Đeni Gobić-Bravar and Daniela Matetić Poljak</i>	899
The Use of Limestone in the Roman Province of Dalmatia <i>Edisa Lozić and Igor Rižnar</i>	915
The Extraction and Use of Limestone in Istria in Antiquity <i>Klara Buršić-Matijašić and Robert Matijašić</i>	925
Aurisina Limestone in the Roman Age: from Karst Quarries to the Cities of the Adriatic Basin <i>Caterina Previato</i>	933
The Remains of Infrastructural Facilities of the Ancient Quarries on Zadar Islands (Croatia) <i>Mate Parica</i>	941
The Impact of Local Geomorphological and Geological Features of the Area for the Construction of the Burnum Amphitheatre <i>Miroslav Glavičić and Uroš Stepišnik</i>	951
Roman Quarry Klis Kosa near Salona <i>Ivan Alduk</i>	957
Marmore Lavdata Brattia <i>Miona Miliša and Vinka Marinković</i>	963
Quarries of the Lumbarda Archipelago <i>Ivka Lipanović and Vinka Marinković</i>	979

Island of Korčula – Importer and Exporter of Stone in Antiquity <i>Mate Parica and Igor Borzić</i>	985
Faux Marbling Motifs in Early Christian Frescoes in Central and South Dalmatia: Preliminary Report <i>Tonči Borovac, Antonija Gluhan and Nikola Radošević</i>	995
INDEX OF AUTHORS	1009

METHODS OF CONSOLIDATION AND PROTECTION OF PENTELIC MARBLE

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Abstract

The purpose of this research study was to investigate the performance of the consolidation and the protective effect of treatments carried out on Pentelic marble specimens exhibiting granular disaggregation. Consolidation materials and techniques were applied and evaluated on weathered samples of Pentelic marble.

“Reinforced lime” and a nano-dispersion of calcium hydroxide were selected as consolidants (with and without sodium stearate) and compared. Before consolidation, the specimens were examined in order to assess their state of conservation, using optical microscopy, infrared spectroscopy (FT-IR) and electron scanning microscopy coupled with microanalysis (SEM-EDX). The consolidation treatments were assessed using SEM-EDX, a portable spectrophotometer, contact angle measurements and sonication treatment in order to study the degree of adhesion with the substrate.

The results showed that the nano-dispersion of calcium hydroxide with the addition of sodium stearate exhibited the best surface consolidation results. It can therefore be applied for both consolidation and protection treatments of Pentelic marble.

Keywords

pentelic marble, calcium hydroxide nano-dispersion, consolidation

1. Introduction

Pentelic marble is a building material of great interest in the field of Monument Protection, as it is used in several monuments throughout the region of Greece. Furthermore, it has been used in monuments and historical building throughout history, ranging from antiquity, dating back to the classical era, up to relevantly recent structures, such as neoclassical buildings. Examples of buildings structured or adorned with Pentelic marble are

of great cultural significance, such as the Acropolis monuments (MARAVELAKI-KALAITZAKI 2005, 187-198), the Hephaistos Temple in the Ancient Athenian Agora (CRAIG, CRAIG 1972, 401-403), the Poseidon Temple in Sounion and more recently the Academy of Athens, the National Technical University of Athens, and other important neoclassical buildings (KORRES 2001).

Pentelic marble was mined from the quarries of the Penteli mountain range. In antiquity the most important quarry was that of “Σπηλιά” located in the southwest part of the Penteli mountain area (MERTZANIS *et al.* 2004, 216). This quarry was in constant use until the 70s when its use was prohibited by law for the minimization of environmental impacts and protection of the area (Greek Legislation Law 386/76) (PAVLOU 1995). Today, the mining of high quality white marble is performed from the quarry of “Διονυσοβούνι” a quarry located at the north extension of the Pentelic mountain range, with the same metamorphic structure (KORRES 2001, 71, 78, 94).

Pentelic marble is well known for its high durability and longevity. Nowadays the Pentelic marble of monuments exposed to heavily polluted environments, such as the atmosphere of Athens’ centre, has become more susceptible to decay, jeopardizing its longevity. The main factors causing the decay of Pentelic marbles are acidic attack, wetting-drying cycles, temperature variation cycles, wind erosion, the presence of salts, incompatible restoration materials and biological attack.

One of the main kinds of decay exhibited by Pentelic marble elements in buildings is granular disaggregation (also called surface sugaring), causing aesthetic problems, but more importantly the loss of cohesion of marble grains on the surface exposed to the environmental factors, leading to crumbling and in some cases detachment of marble elements. Granular disaggregation is due to environmental factors, such as temperature variations and acid rain as well as endogenous factors, such as the anisotropy of the material itself. Granular disaggregation is triggered by environmental thermal excursions, such as day/night variations (especially for marble elements directly exposed to solar radiation). Temperature

variations cause deformation of calcite crystals, due to their unusual anisotropic behavior; they expand parallel to the crystallographic *c*-axis and contract perpendicularly to the same axis. As a result, micro-cracks open at the boundaries between grains that consequently lose cohesion and become prone to detachment. This latter aspect further threatens marble durability, because, through the newly developed micro-cracks, clean and acid rainwater, salt-rich rising damp, as well as atmospheric gaseous pollutants, can penetrate into the marble, thus exacerbating the related weathering phenomena (e.g., calcite dissolution, gypsum formation and salt crystallization) (SASSONI, FRANZONI 2014, 1893-1906; SASSONI, GRAZIANI, FRANZONI 2015, 1145-1157).

Several materials have been used in the past for the consolidation of marble surfaces. A suspension or a solution of barium hydroxide, sometimes with the addition of calcium hydroxide or urea has been used in the past for the consolidation of stones and marbles. Barium hydroxide, reacting with the carbon dioxide in the atmosphere, is transformed into barium carbonate and water. Some studies concerning barium hydroxide initially showed good results; however the sedimentation of the newly formed crystals was confined to the outer surface layers, leading to flaking in contact with the atmosphere; low connection capability between the stone particles (grains, crystals) ranks highly among its drawbacks. Casein and its products have also been used in the past for the consolidation of marble, however its presence induces surface bio-colonization and therefore extensive biological attack of the marble surface (SKOULIKIDIS 2000, 23-25; SKOULIKIDIS, VASSILIOU, TSAKONA 2005, 28-33).

Organic polymeric consolidants have been used in recent years, however they are considered completely unsuitable for marble consolidation; stability and durability are the main issues, which make organic polymeric treatments generally unsuitable for marble consolidation, in addition to their lack of chromatic compatibility (SASSONI, FRANZONI 2014, 1893-1906).

Silicate consolidants, such as ethyl silicate, are reported to provide a good immobilization of calcite grains, thanks to the deposition of silica gel in intergranular fissures. However, no chemical bonding between silica gel and marble occurs, with scarce mechanical improvement and effectiveness over time (SASSONI, GRAZIANI, FRANZONI 2015, 1145-1157).

More recently, researchers have examined the use of ammonium oxalate (AmOx) treatments. AmOx treatments were first employed in order to make the surface it was applied to acid-resistant through a passivating treatment, by the formation of calcium oxalate, through the reaction of AmOx with the calcite of the marble. This is considered particularly advantageous and important

in the case of porous calcareous materials exposed outdoors, particularly in polluted urban centers. Although encouraging results have been reported regarding the efficacy of AmOx, calcium oxalate formation has been found to be patchy on the marble surface and further research is required (MATTEINI 2008, 13-27; CHAROLA, CENTENO, NORMANDIN 2010, 29-44).

Sassoni *et al.* proposed the use of ammonium phosphate in order to form hydroxyapatite (HAP) inside marble micro-cracks. The results of the study indicate remarkable consolidation of weathered marble, with only slight alterations in pore size distribution and color change, thus providing much better results than either ethyl silicate or ammonium oxalate. However, studies regarding HAP nucleation and growth over calcite have pointed out that the effectiveness of the HAP coating to prevent dissolution of marble is partially limited by the HAP layer porosity and incomplete coverage of the marble surface (SASSONI, GRAZIANI, FRANZONI 2015, 1145-1157).

Lime-based consolidants are compatible and have been extensively used until the present. When calcium hydrate comes in contact with the atmosphere's carbon dioxide, it is transformed into calcite (a part of which is aragonite); this is the reason for lime-based consolidants being ranked very high amongst the consolidation materials used for calcite stones and marble surfaces. The product of the reaction is chemically and crystallographically similar to the calcium carbonate of marble; however it presents microstructure characteristics and mechanical properties different to the calcium carbonate of marble. The use of lime however presents disadvantages; it presents a very low carbonation rate, carbonation is not extended in the depth of the material and even when carbonation is complete, the mechanical strength and hardness values are quite low. According to Skoulikidis *et al.* the disadvantages of lime are overcome with the use of "reinforced lime", namely the addition of limestone powder, which accelerates the reaction; the addition of 6% CaCO₃ to plain lime increases the poor mechanical resistance of the CaCO₃, (produced by the reaction of atmospheric CO₂ and the lime), because of the acceleration of the reaction and the subsequent small crystals of CaCO₃ and facilitates the precipitation of CaCO₃ to the bulk of the mass of lime (SKOULIKIDIS, VASSILIOU, TSAKONA 2005, 28-33).

Caner observed that the addition of sodium stearate in low concentrations to a nano-dispersive calcium hydroxide solution increased the size and shape of calcite particles formed and facilitated efficient bonding in the cracks of the limestone consolidated, without affecting the stability of the solution (CANER 2011, 89, 109).

In this research study the performance of the consolidating and protective effect of treatments carried out on Pentelic marble specimens was investigated.

Consolidation materials		
	Alcohol-based nano- dispersion of Ca(OH) ₂	Suspension of calcium hydroxide, 6% p.w. CaCO ₃
Without sodium stearate	MP(A)	
	OR(A)	
With 90 mg/l sodium stearate	MP(E)	
	OR(E)	
Without sodium stearate		MP(B)
		OR(B)
With 90 mg/l sodium stearate		MP(F)
		OR(F)

Fig. 1.
Consolidation
treatments

Consolidation materials and techniques were applied and evaluated on samples of Pentelic marble, deriving from two different restoration periods of the early and mid-20th century. The consolidation materials selected were one traditional type, currently used in the restoration of Pentelic marble, and one novel nano-material in order to compare their effectiveness.

2. Materials and methods

2.1. Sample description

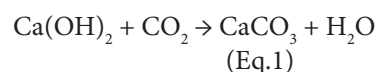
The samples used in this experimental study were Pentelic marble specimens from two different restoration periods and present granular disaggregation. The first restoration work was in the early 20th century. These samples are coded MP and the sample dimensions were 1.35 cm x 3 cm x 1 cm ±1 mm. The second restoration period was in the mid-20th century. These samples are coded OR and the sample dimensions were 2 cm x 4 cm x 0.8 cm ±1 mm. All samples used were exposed outdoor until present to the polluted atmosphere of Athens and to environmental factors, the same factors affecting many monuments of the Athens center.

2.2. Consolidation materials and techniques

Two consolidation materials were selected in order to compare their effectiveness; a solution of hydrated lime with the addition of 6% p.w. CaCO₃ (reinforced lime), used until today, and an application of a novel nano-dispersion of calcium hydroxide, in a concentration of 15 g/l. Furthermore, the effect of the addition of sodium stearate (sodium stearate: C₁₇H₃₅CO₂Na) was

examined by the addition of 90 mg/l to both materials for some applications (Fig. 1), in order to validate whether its use will assist in better formed calcite particles and facilitate efficient bonding. In order to ensure a homogeneous and reproducible dispersion, the calcium hydroxide nano-dispersion was sonicated in a sonication device (VCX 750 της εταιρείας SONICS & MATERIALS, INC). The addition of sodium hydroxide was also followed by sonication with the same device.

The reaction leading to consolidation is the same for both materials:



The application of the consolidation treatments was conducted via spray applications, in order to simulate real treatment conditions. The spray application was done at a 15 cm distance from the marble surface. The nano-dispersion consolidation treatments (A&E) were applied 2 per week for 14 days (4 treatments in total), whereas the reinforced lime treatments (B&F) were implemented 2 per day for 20 days (40 treatments in total, as done in current practice). The total number of applications was calculated for each material in order for the total quantity of deposited lime to be comparable.

The treated samples were put in a vessel with 75% relative humidity for two months (supersaturated solution of NH₄Cl) in order to ensure the complete carbonation of the treated samples and the conversion of the calcium hydroxide to calcite (GOMEZ-VILLALBA, LOPEZ-ARCE, ALVAREZ DE BUERGO 2011, 1249-1254; CANER 2011, 109).

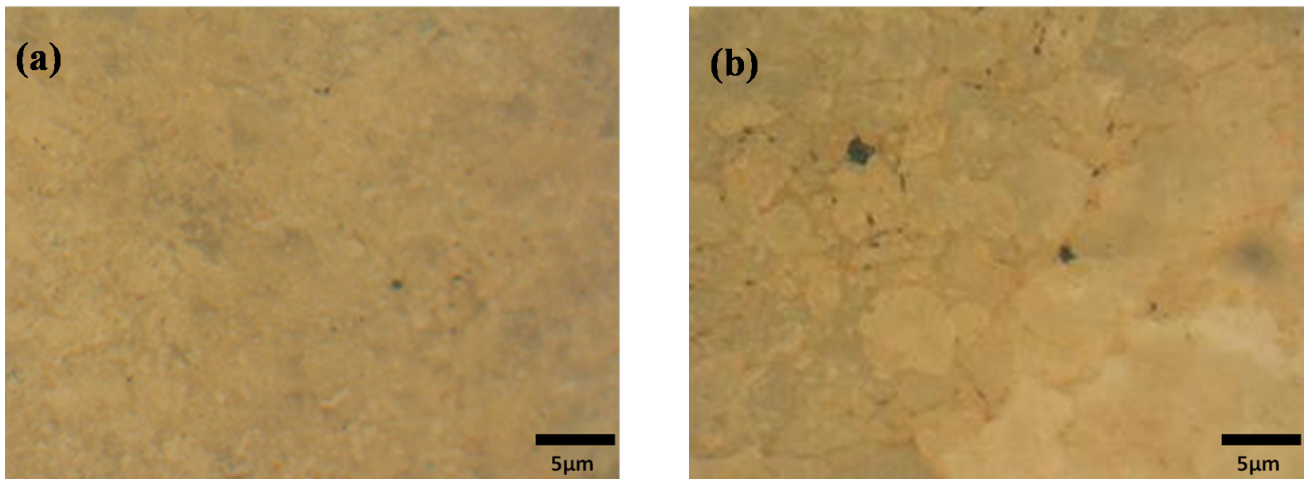


Fig. 2. Optical microscopy images of both marble sample types before consolidation treatments, a) MP x120, b) ORx120

2.3. Evaluation techniques

All samples were examined before the application of the selected consolidation treatments, in order to examine their state of conservation and the main exhibited decay, as well as after the consolidation treatments, in order to assess their efficacy.

Before the application of the consolidation treatments, the specimens were immersed in deionized water in order to remove dirt, loose deposits and gypsum (WT). The surface of the marble samples (WT) was then examined microscopically via optical digital microscopy (Scopeman Moritex microscope) and via stereomicroscopy (Leica MZ6). Scanning Electron Microscopy (SEM-EDX) was employed in order to examine the untreated marble surface and detect the type of decay of the specimens. The scanning electron microscope used was a Quanta 200 Fei and the acceleration voltage during the procedure was 25-30 KV. The software EDX Genesis was used for the X-ray microanalysis. Infrared spectroscopy (FT-IR) was conducted in order to detect decay products on the marble surface, through the analysis of a small amount taken from the marble surface (FT-IR Biorad Excalibur FTS 3000MX).

Microscopic examination of the marble surfaces was performed after the consolidation treatments in order to assess the effectiveness of the treatments and the state of the consolidated surface, as described above. SEM-EDAX was conducted in order to examine the consolidated surface and the consolidation products, as well as to determine whether the consolidation treatments resulted in any unwanted and possibly harmful by-products. All samples were weighed before (W_{initial}) and after the consolidation treatments (W_{final}), in order to estimate the mass gain due to consolidation and calcite crystal formation.

Furthermore, a portable spectrophotometer was used before and after the treatments in order to evaluate the variation of the chromatic parameters adopting the CIE Lab system (Dr Lange Color Pen LMG 159/160).

The applied consolidation treatments were also assessed through contact angle measurements, in order to examine whether the applied treatments resulted in a change of the contact angle. Contact angle measurements were conducted with untreated (WT) and consolidated specimens in compliance with EN 15802:2010.

The adhesion degree of the consolidation materials with the marble substrate was studied through sonication treatments. The consolidation effect of the proposed treatments was assessed via sonication tests (RODRIGUEZ-NAVARRO *et al.* 2003, 2182-2193; DASKALAKIS *et al.* 2013, 409-423; DASKALAKIS *et al.* 2015, 73-84). Consolidated samples as well as untreated samples were immersed in deionized water in an upright position. Sonication occurred for 5min (20 KHz, Emmi 30 HC EMAG) and the samples were immediately rinsed with deionized water and dried at 60 °C for 24 h prior to weighing. The process was repeated five times. Results are presented as weight loss per cycle ($W_{i-1} - W_i$; i:cycle number). The weight of each sample was measured before each sonication cycle (W_{i-1}) and after each sonication cycle (W_i).

3. Results and discussion

3.1. State of preservation

The untreated marble samples (WT) were first examined in order to evaluate their state of preservation. The main type of decay detected through optical microscopy was the extended granular disaggregation on the surface of the marble specimens (Fig. 2a, Fig. 2b). All MP specimens, although exposed to the environment at

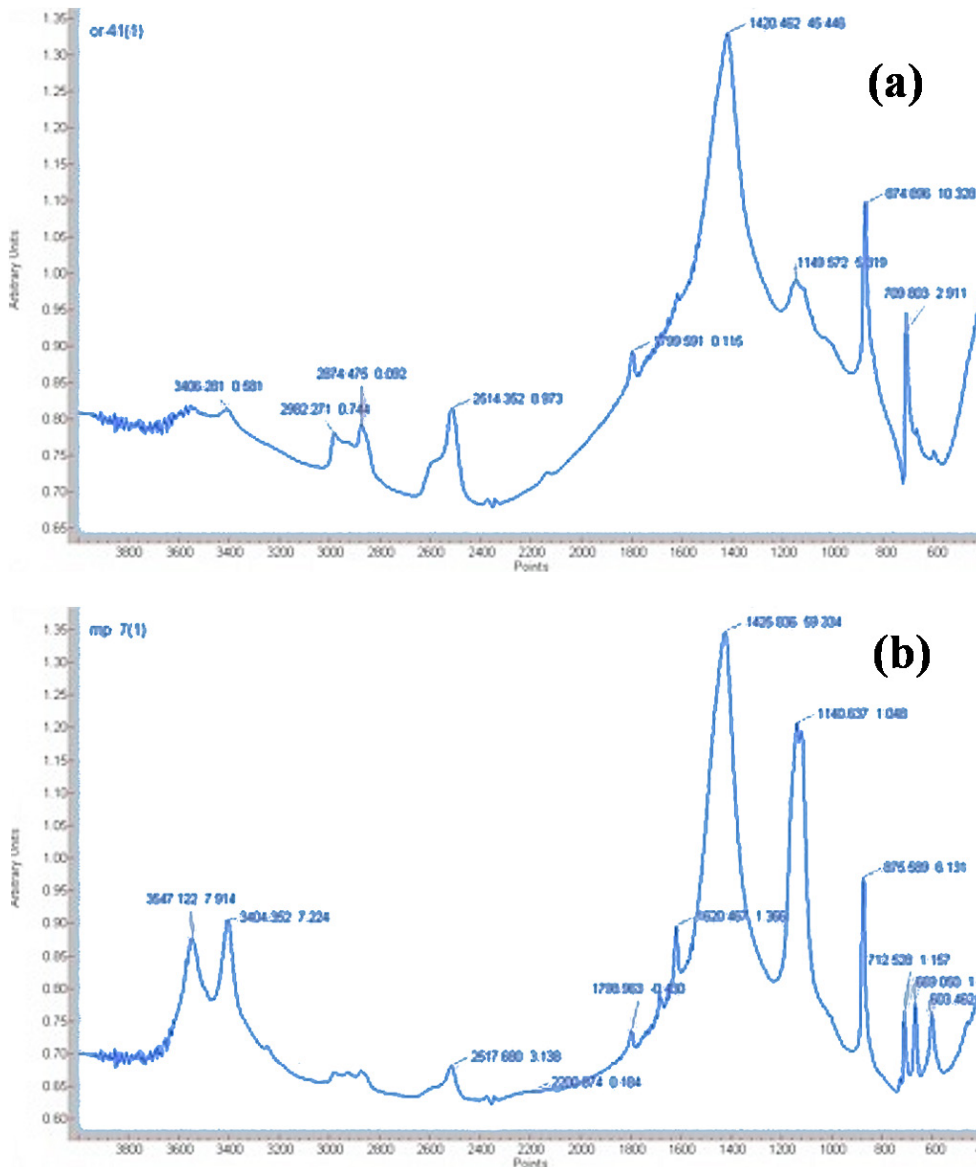


Fig. 3.
FT-IR results,
a) FT-IR results for
marble samples MP,
b) FT-IR results for
marble samples OR

least three decades more than the OR specimens, show a better state of preservation. This can be attributed to the different exposure conditions. Bio-deterioration was noticed in all samples.

FT-IR was employed in order to identify decay products on the marble samples (Fig. 3a, Fig. 3b). Gypsum was detected in all samples, both MP and OR, due to the sulphation process, generated from the polluted urban environment the samples have been exposed to for decades. Organic compounds are also detected probably due to the hydrocarbons of the urban atmosphere.

Scanning Electron Microscopy (SEM) confirms the optical microscopy results regarding the main type of decay, as granular disaggregation is observed throughout the surface (Fig. 4). Microanalysis via EDAX showed traces of sulphur and lead, as well as a small percentage of alumino-silicate contaminants (Fig. 4). The alumino-silicate contaminants are generated from the material itself

or deposited from the atmosphere, and the traces of lead are probably due to the sealing with lead in the procedure since ancient times.

3.2. Assessment of consolidation treatments

The marble specimens were evaluated after the consolidation treatments. From the microscopic examination (SEM) the inhomogeneous distribution of the neo-formed calcite crystals on the surface of the samples treated with the reinforced lime (Treatments B&F) was noticed; the formed crystals present a different size and shape from the original marble crystals (Fig. 5a). The samples treated with the nano-dispersion of calcium hydroxide (A&E) presented an improved deposition covering the entire marble surface; the formation of calcite crystals is homogeneous and the formed calcite crystals present a better adhesion to the marble surface, covering the intercrystalline voids

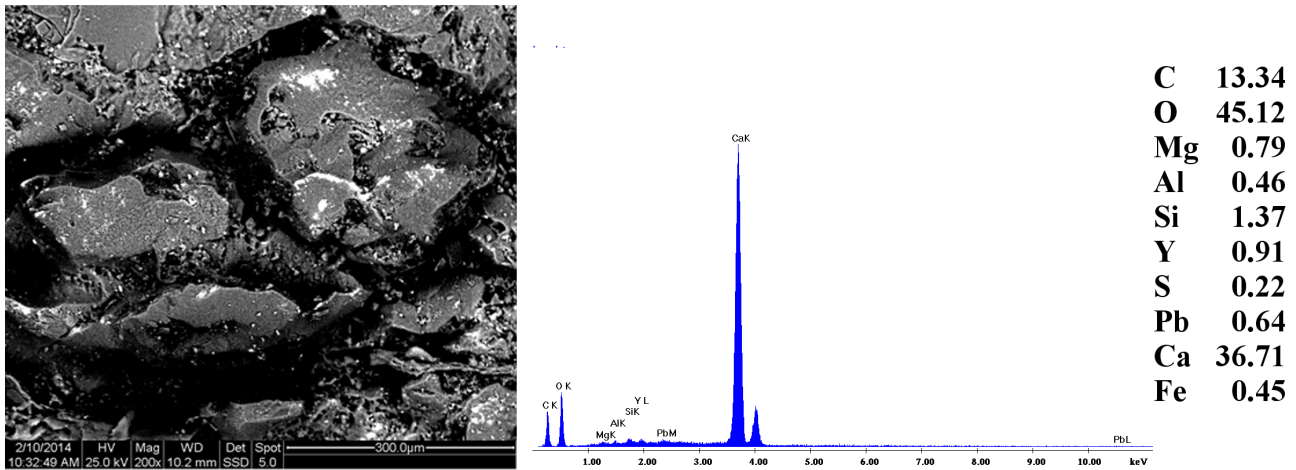


Fig. 4. SEM-EDX results of untreated samples (WT)

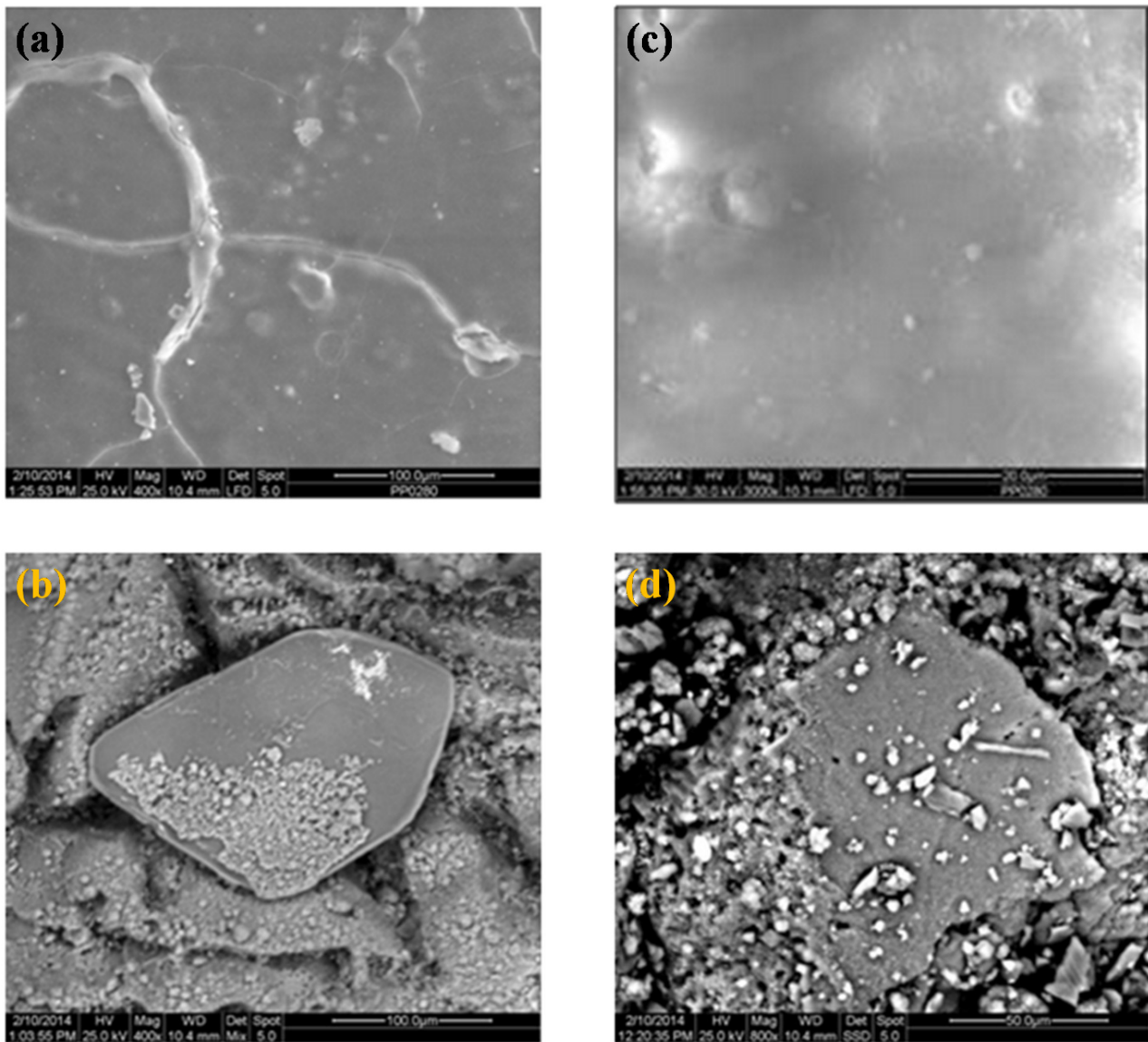


Fig. 5. SEM images of consolidated marble samples, a) SEM image of OR sample consolidated with (A) treatment x400, b) SEM image of OR sample consolidated with (B) treatment x400, c) SEM image of OR sample consolidated with (E) treatment x3000, d) SEM image of OR samples consolidated with (F) treatment x800

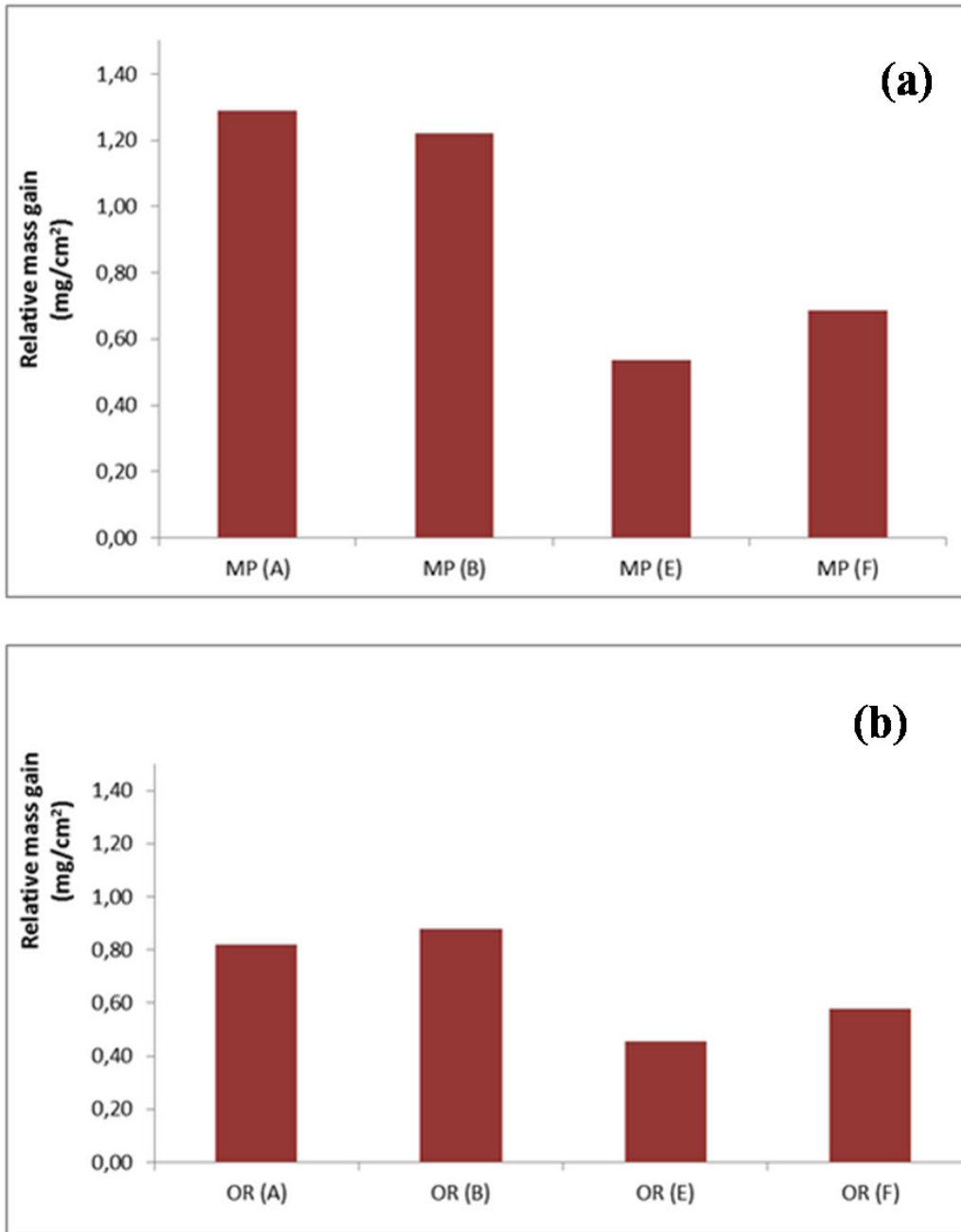


Fig. 6. Relative mass gain due to consolidation treatments: a) Relative mass gain (mg/cm²) due to consolidation treatments on MP samples, b) Relative mass gain (mg/cm²) due to consolidation treatments on OR

(Fig. 5b). Furthermore, the use of sodium stearate along with nano-dispersion of calcium hydroxide reduces considerably microcracking and results in an even more homogenous consolidated surface (Fig. 5c).

All marble specimen masses were measured before the consolidation treatments and after the consolidation treatments, in order to determine the relative mass gain exhibited due to the applied consolidation treatment (after complete carbonation). The results are presented in Fig.6 as relative mass gain and have been derived from the weight gain exhibited by each sample in relation to the total consolidated surface (g/cm²). The samples treated with reinforced lime (Treatments B&F) exhibit a quite similar mass gain, with small deviations,

to the samples treated with the nano-dispersion of calcium hydroxide (A&E). When the treatments were applied without the addition of sodium stearate (A&B) they presented a greater mass gain than the treatments applied with the addition of sodium stearate (E&F).

Sonication treatments were employed in order to examine the degree of adhesion of the consolidation materials. Sonication tests proved that all treatments increase the cohesion of the marble surface, in comparison to the untreated specimens, thus resulting in a more solid marble surface, withstanding sonication forces. Results here are presented as the cumulative weight loss in relation to sonication cycles for consolidated marble samples. In particular, as seen in Fig. 7a and Fig. 7b, the improvement

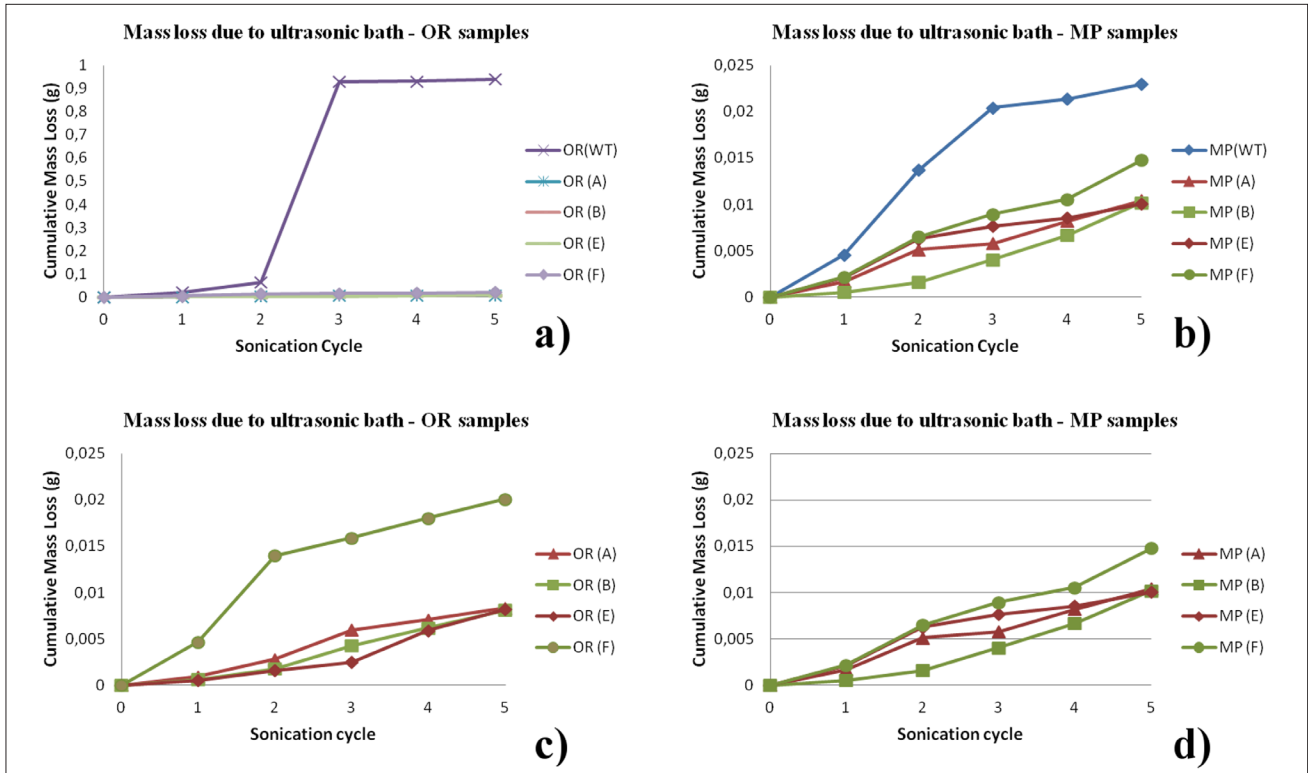


Fig. 7. Cumulative mass loss (g) due to ultrasonic bath treatments by cycle, a) OR samples treated and untreated, b) MP samples treated and untreated, c) OR samples only treated, d) treated MP and OR samples comparison

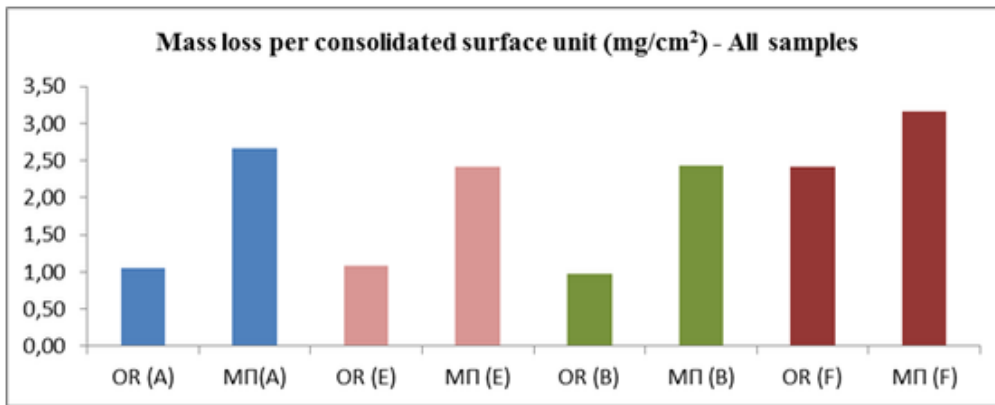


Fig. 8. Total mass loss per consolidated surface at the end of the sonication cycles (mg/cm²)

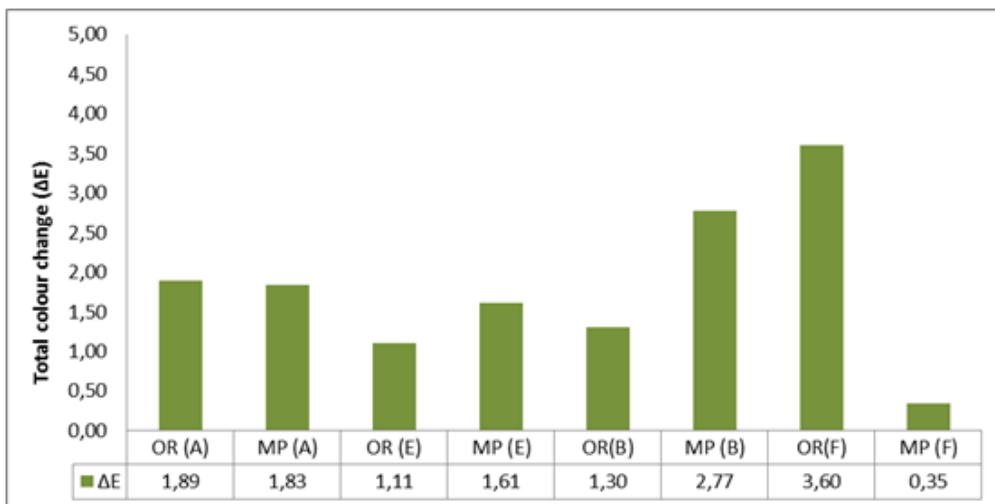


Fig. 9. Total color variation for all treated samples (ΔE)

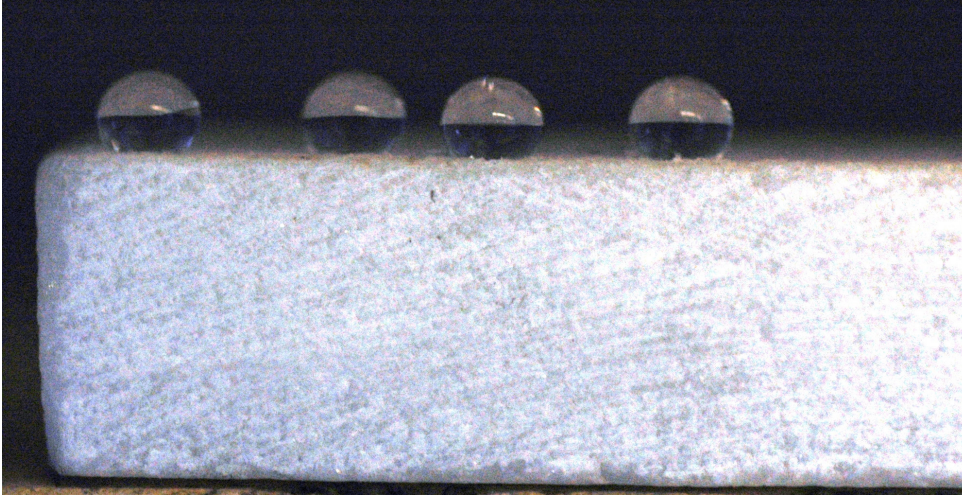


Fig. 10.
Static contact angle
measurements

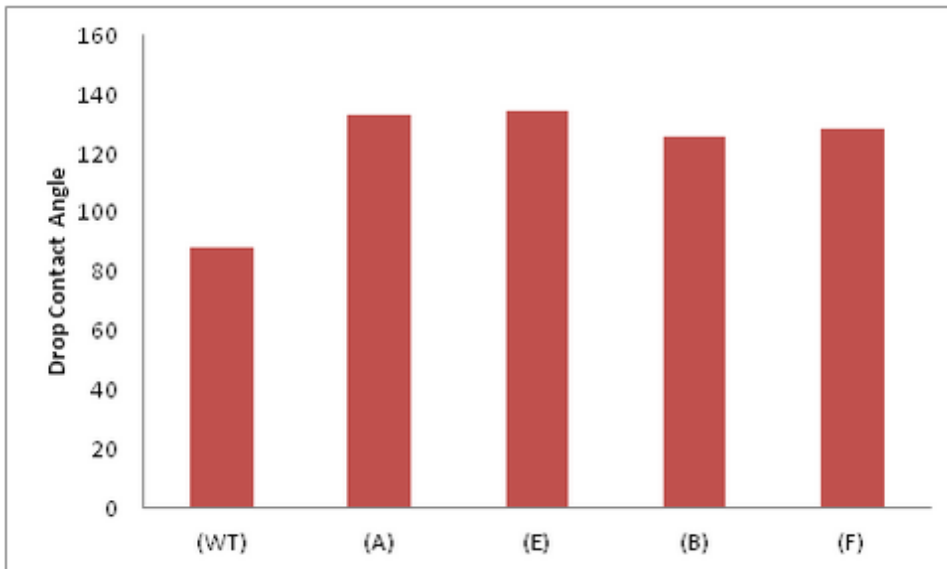


Fig. 11.
Drop contact angle
measurements for untreated
marble sample (WT) and
consolidated samples

to the cohesion of the samples' surface is considerable, especially for samples OR, which were in a worse state of preservation than the MP samples. In general, as shown in Fig. 7b and Fig. 7c it seems that the addition of sodium stearate does not have a beneficial effect on the mass loss measured, especially in the case of reinforced lime (B&F), where samples treated with reinforced lime exhibit a lower mass loss than samples treated with the solution of reinforced lime and the addition of sodium stearate. Both consolidation treatments have a larger impact on the OR samples, which were in a worse state of preservation before the applied treatments (Fig. 7d). Furthermore, as seen in Fig. 8, the OR samples present a lower total mass loss per surface than the MP samples, indicating that the consolidation treatments are more effective on surfaces presenting a higher degree of granular disaggregation.

Colorimetric measurements were taken before and after each consolidation treatment in order to examine the chromatic variations that each consolidation

material induced. All samples presented total colour difference values lower than 5 (Fig. 9) and are considered acceptable. A consolidation treatment can be considered acceptable if the total colour change (ΔE) is less than 5 (DELGADO RODRIGUES 2007, 32-43). The same treatments seem to induce a different colour change with different degree of decay; for example, treatment (F) induces an extremely low colour change on MP samples and a relatively high colour change on samples OR. The use of the nano-lime dispersion (E) presents the lowest colour change for both sample types.

Static contact angle measurements were carried out before and after the consolidation treatments (Fig. 10). In all samples the contact angle increased after treatment, resulting in values over 90° in all cases. The samples consolidated with the novel nano-dispersion of calcium hydroxide (A) exhibited contact angle almost 10° higher than the samples consolidated with the reinforced lime (B). The use of reinforced lime with the addition

of sodium stearate (F) results in slightly higher contact angle, however still lower than the contact angle exhibited by the samples consolidated with the novel nano-dispersion of calcium hydroxide (A). The highest values of static contact angle were exhibited by the samples treated with the nano-dispersion of calcium hydroxide with the addition of sodium stearate (E), thus having protective effect on the marble surface (Fig. 11).

4. Conclusions

The consolidation treatment with the nano-dispersion of calcium hydroxide presented a better total performance than the current traditional consolidation treatment with reinforced lime. The samples treated with reinforced lime, with and without the addition of sodium stearate presented an inhomogeneous distribution of the neo-formed calcite crystals on the surface of the samples; the formed crystals present a different size and shape than the original marble crystals. The samples treated with the nano-dispersion of calcium hydroxide (A) presented an improved deposition covering the entire marble surface, the formation of calcite crystals is homogeneous and the formed calcite crystals present a better adhesion to the marble surface; furthermore, the addition of sodium stearate to the nano-dispersion (E) diminishes micro-cracking and at the same time increases the contact angle, thus also having a higher protective effect on the marble surface.

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