$Ca(OH)_2$ nanoparticle characterization: microscopic investigation of their application on natural stones

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Abstract

Owing to conversion of lime into calcium carbonate, lime is usually adopted for conservative surface treatments. However, some critical aspects concerning the treatments reduced penetration depth, the binder concentration and the incomplete lime carbonation process still represent undesired limits and hindrances. In order to improve lime treatments, $Ca(OH)_2$ particles with nanometric dimensions (*nanolime*) have recently been introduced in Cultural Heritage conservation (frescoes, stuccoes, ..). The aim of the present work is to characterize $Ca(OH)_2$ nanoparticles synthesized by a chemical precipitation process starting from two base supersaturated aqueous solutions of calcium chloride and sodium hydroxide. After several washes, necessary to remove the sodium chloride, the aqueous medium is partially substituted by 2-propanol to improve the suspension stability; an alcoholic nanolime suspension is obtained, characterised by a given concentration and a residual water content. In order to identify the structure of the formed phases and the particles reactivity, the obtained nanolime is characterised by X-ray diffraction (XRD) and profile analysis; scanning and transmission electron microscopy (SEM-TEM) are performed too. The results show hexagonally plated and regularly shaped particles with side dimensions equal to or less than 300nm; moreover particles have pure crystalline features and a high reactivity in terms of the carbonation process. Finally, the $Ca(OH)_2$ nanoparticles are applied on some natural lithotypes; SEM analyses are performed to evaluate penetration depth and grain adhesion of the nanolime treatments itself. From SEM micrographs a partial filling of the lithotypes pores, located at a distance from the surface of more than 200µm, is observed.

Keywords: calcium hydroxide, consolidation, lime, nanoparticles, protection.

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1 Introduction

Thanks to conversion of lime into calcium carbonate, lime water and milk are usually adopted for conservative surfaces treatments. In particular, lime water consolidation is generally obtained spraying the lime solution on the cleaned surface. To reach a good penetration, the treatment is repeated several times until the surface is able to absorb lime water [1]; some Authors indicate that could be necessary to repeat the application for 30-40 times [2]. Lime milk is used on the same basis as lime water [3]; nevertheless it involves greater amounts of lime with the same water volume, reducing the water percentage brought to the stone. However, some critical aspects concerning the treatments reduced penetration depth, the binder concentration and the incomplete lime carbonation process still represent undesired limits and hindrances. In order to improve lime treatments, $Ca(OH)_2$ particles with submicrometric dimensions (*nanolime*) are recently introduced in Cultural Heritage conservation. Lime nanoparticles present the following advantages in stone, mortar and plaster consolidation: the possibility to penetrate deep into damaged zones (no limitations due to the particle size), high reactivity and fast reactions (such as carbonation) in the treated zones, high purity and defined composition [4]. *Nanolimes* are successfully employed on mural paintings, stuccoes and frescoes [5–9]; refurbishments of architectonical surfaces are considered too [10–12]. Lime nanoparticles are typically produced by a chemical precipitation process in supersaturated aqueous solutions of the reactants (calcium chloride and sodium hydroxide). To improve nanolime particles dispersion, the use of alcoholic solutions in place of aqueous ones is adopted; in fact, when 2-propanol alcohol is used as a solvent, dispersions of calcium hydroxide particles show a slower rate of agglomeration (and therefore, slower sedimentation rates) in comparison to aqueous media. This reduces the tendency for a white film to form on surfaces to be consolidated [13].

In this paper a nanolime suspension, characterised by a residual water content in the precipitated phase, is synthesised. X-ray diffraction (XRD) measurements and profile analysis are performed to characterise the nanolime samples and to evaluate the carbonation efficiency (*yield*). To correlate the produced nanolime to its properties, morphological characterisation is performed by scanning and transmission electron microscopy (SEM and TEM).

Finally, the nanolime suspension is applied by brush on cleaned stone surfaces of natural lithotypes; in particular, the suspension is used in a diluted form (concentration of about 1mg/ml) in order to avoid the risk of leaving a white film on treated materials surfaces [11].

Several lithotypes, largely employed in architectonic fields, are considered: *"Travertine", "Pietra di Lecce", "Pietra Serena"* and *"Basalto"*.

A local calcareous lithotype, *"Poggio Picenze"* is investigated too. SEM analyses allow one to investigate how the nanolime penetrates inside the stone porosity, in terms of the reached depth and the grains adhesion of nanolime treatments itself.

2 Experimental section

Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), sodium hydroxide (NaOH) and 2-propanol *pro analysi* products, supplied by Merck, are used without further purification. Water is purified by a Millipore Organex system ($R \geq 18$ MΩ cm).

Two aqueous solutions of 400ml, containing 0,3mol/l of $CaCl_2$ and 0,6mol/l of NaOH respectively, are prepared. The NaOH solution (used as precipitator) is added dropwise into the $CaCl_2$ solution (speed ≈ 4ml/min, temperature of 90°C). After about 24 hours two distinct phases are observed: a limpid supernatant solution and a white precipitated phase (NL_W sample). In order to remove the NaCl produced, several deionised water washings are performed. Subsequently, in order to improve the suspension stability, the water content is partially substituted by 2-propanol; the obtained suspension is characterised by a water/2-propanol ratio (W/A) of 0,75 and a final concentration of about 10mg/ml (NL_A sample). SEM analyses (*Philips XL30CP*) are performed, depositing 0,2ml of the suspension on the specimen; TEM investigations (*Philips CM100*) are carried out dispersing 0,2 ml of the suspension in 50 ml of 2-propanol and depositing the sample on the suitable grid.

As concerns XRD measurements, the sample is prepared maintaining the nanolime preparation for 20’ in ultrasonic bath (US) and then depositing 0,2ml of the suspension on a silica sample holder; measures are performed on dry sample, in laboratory conditions (T=20°C, relative humidity RH=40%). Each experimental diffraction spectrum is elaborated by a Profile Fit Software (*Philips PROFIT v.1.0*) and each crystalline phase is attributed by JCPDS patterns; the ratio between the $CaCO_3$ peaks area and the spectrum total area is assumed as the carbonation process efficiency (*yield*).

2.1 Results and discussions

TEM micrographs, obtained on NL_A sample, are reported in Fig.1; in particular, hexagonally and regularly shaped particles of side dimension ranging from 100 to about 300nm are observed. Moreover, in Fig.1b) it is possible to note that all the particles appear overlapped in an ordered way and are so thin to be transparent to the electron beam.

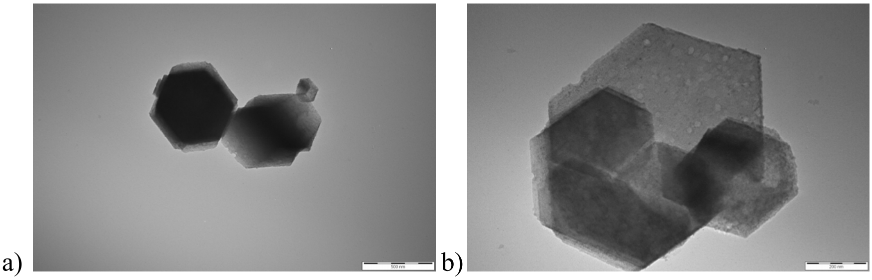

Figure 1: TEM micrographs on NL_A sample: a) scale bar 500nm; b) scale bar 200nm.

In Fig. 2, SEM images on NL_A sample are shown. The particles, characterised by a prismatic features are recognizable to calcium carbonate of side dimension less than 500nm (Fig.2a). In Fig.2b) a perfectly hexagonal and regular shaped particle (marked as A) is observed, characterized by a side dimension less than 250nm.

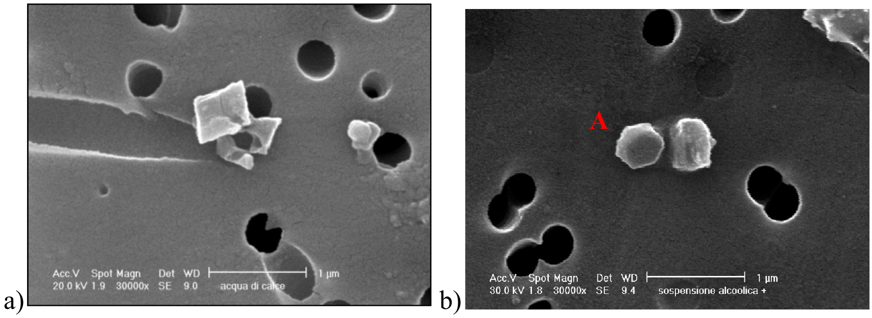

Figure 2: SEM micrographs on NL_A sample (scale bar 1μm).

XRD pattern on NL_A sample shows the presence of $Ca(OH)_2$ and $CaCO_3$ phases (84-1276 and 85-1108 JCPDS patterns, respectively) with a corresponding *yield* value of about 80% (Fig.3a). On the contrary, XRD results obtained on NL_W sample show as the corresponding *yield* decreases, reaching a value of about 50% (Fig.3b). The NL_A higher *yield* values can be attributed to the presence of 2-propanol, that tends to “disagglomerate” the nanolime particles; so, a greater specific surface of the $Ca(OH)_2$ particles exposed to air, can leads to a better carbonation process.

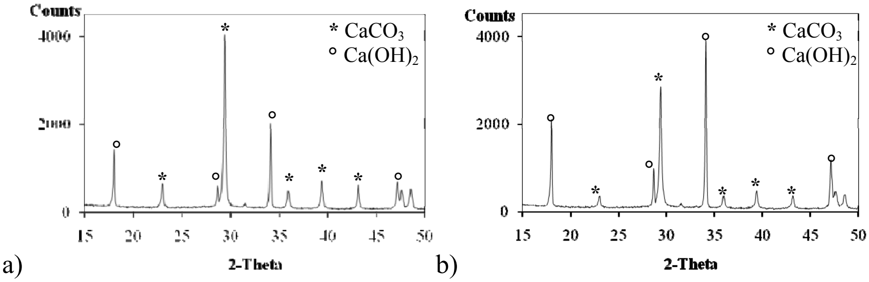

Figure 3: XRD patterns: a) NL_A sample; b) NL_W sample.

3 Treatment on natural lithotypes: characterisation and results

The considered samples, largely employed in the Italian historical architecture, are natural calcareous stones - *Travertine*, *Pietra di Lecce* and *Poggio Picenze* (the last one is a local lithotypes), a national sandstone - *Pietra Serena* - and an igneous lava stone of volcanic origin - *Basalto*.

The nanolime treatment is carried out by brush, in laboratory conditions (T=20°C; R.H. 50%), applying the diluted alcoholic suspension (characterised by a concentration of 1mg/ml) on the dry and clean stones surface. In particular, 1ml of the suspension is applied on a side ($5*5cm^2$) of the stone surface; when the solvent is evaporated, this procedure is repeated for 100 times (giving about 100mg $Ca(OH)_2$ for each stone). For SEM investigations, each stone sample is broken along a plane perpendicular to the treated side and the section surface is observed. On the following figures, SEM micrographs, referred to untreated and treated samples section, are shown; in particular, in order to evaluate the treatment penetration inside the stone, pores situated at different surface distances are considered.

3.1 Travertine

In Fig. 4 SEM micrographs on untreated *Travertine* stone sample is reported; in particular, a typical region, containing macropores and areas with a compact matrix is shown. For what concerns the treated stone, it is possible to note as the nanolime treatment covers the internal stone pore without filling it completely (Fig.5). In particular, the treatment, well recognisable in SEM micrograph referred to a pore at 150μm from the surface (Fig.5a-b), is found also in pores located at about 1mm from the surface itself (Fig.5c-d). This result can be attributed to the Travertine porosimetric structure, constituted by macropores, by which the nanolime treatment can be carried inside the stone.

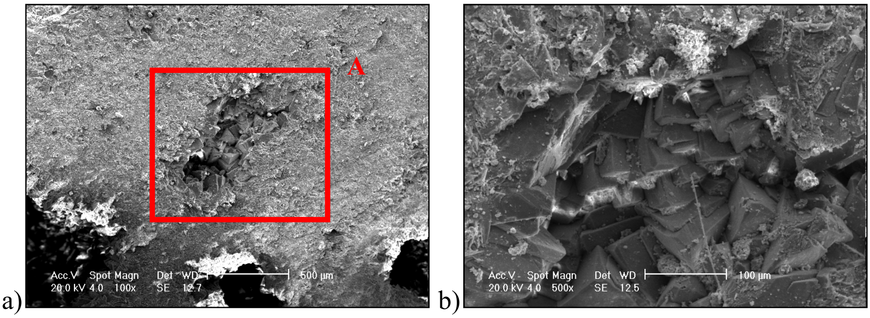

Figure 4: SEM micrographs on untreated Travertine stone: a) sample section (scale bar 500μm); b) zoom view on **A** pore (scale bar 100μm).

3.2 Lecce stone

Pietra di Lecce is an organogenic marl calcareous stone, compact, generally porous and characterised by a fine-grained structure [14]. In Fig. 6, SEM micrographs on untreated sample are reported; it is possible to note the granular stone structure, constituted by various size clasts and by an intergranular porosity (Fig.6b).

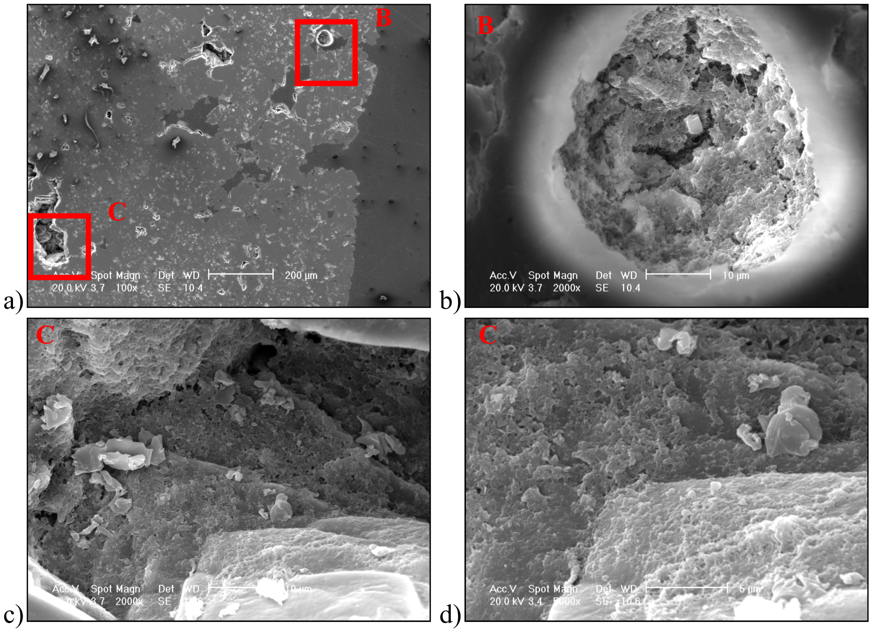

Figure 5: SEM micrographs on treated Travertine stone: a) sample section (scale bar 200µm); b) zoom view on **B** pore localised at 150µm from the surface (scale bar 10µm); c)-d) different zoom views on **C** pore at about 1mm from the surface (scale bar 10µm and 5µm, respectively).

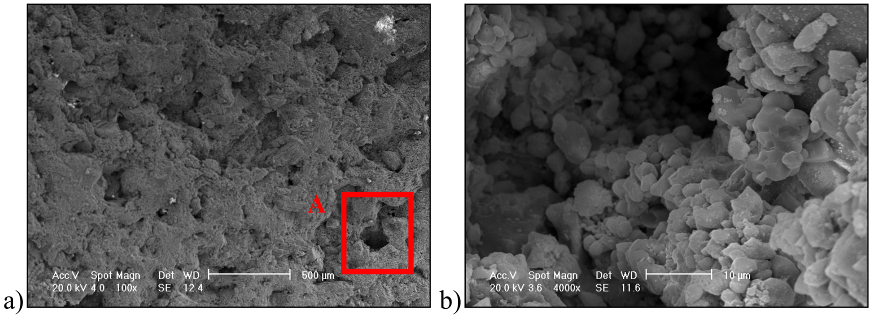

Figure 6: SEM micrographs on untreated Lecce stone: a) sample section (scale bar 500µm); b) zoom view on **A** pore (scale bar 10µm).

Considering the treated sample, the treatment covers homogeneously the internal stone pores without filling them completely (Fig.7b-c). In particular, the treatment is also well recognisable in the pore located at 800µm from the surface, underlining the penetration depth reached from the treatment itself (Fig.7c).

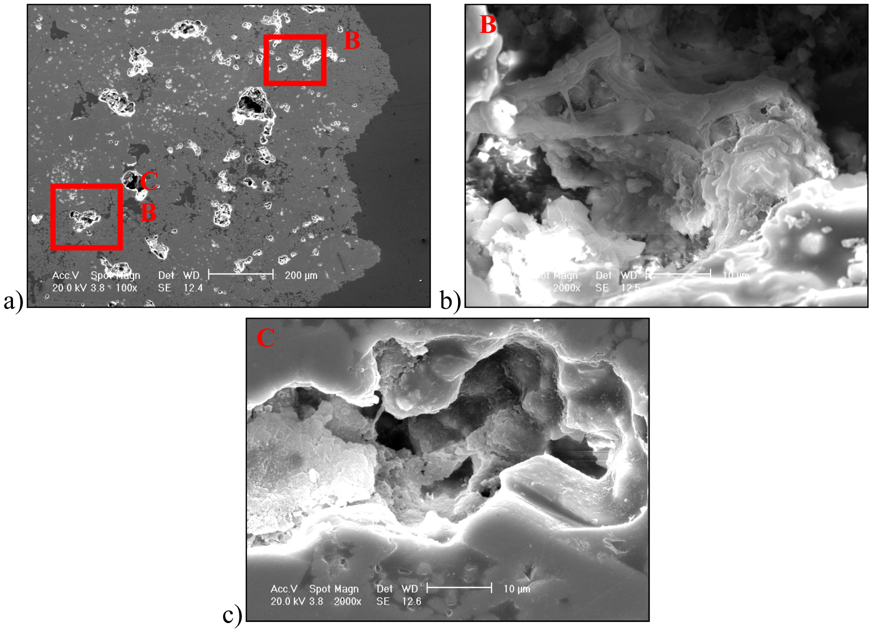

Figure 7: SEM micrographs on treated Lecce stone: a) sample section (scale bar 200µm); b) zoom view on **B** pore localised at 250µm from the surface (scale bar 10µm); c) zoom view on **C** pore at about 800µm from the surface (scale bar 10µm).

3.3 Poggio Picenze stone

Poggio Picenze lithotype, a local calcareous stone, is constituted by heterogeneous grained material; the stone surface and its internal structure are characterized by small-medium size pores and vacuoles (Fig.8) [14].

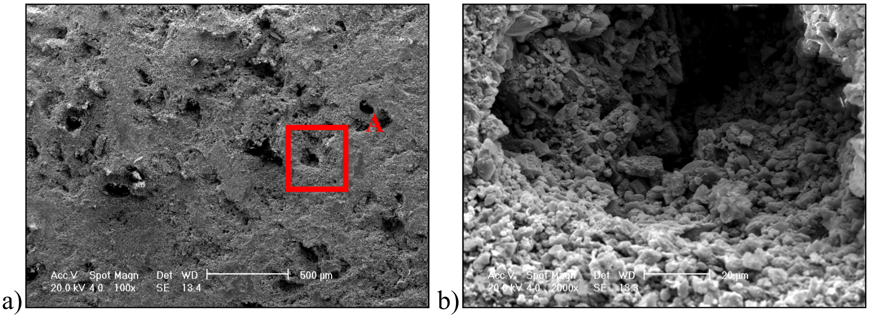

Figure 8: SEM micrographs on untreated Poggio Picenze stone: a) sample section (scale bar 500µm); b) zoom view on **A** pore (scale bar 20µm).

SEM micrographs referred to treated stone, show as the nanolime treatment tends to fill the internal cavity of the material, adhering to its grain, without occlude the pores. In particular, the treatment, recognisable in a pore located at a distance of 300µm from the surface (Fig.9), is not found in more internal cavities.

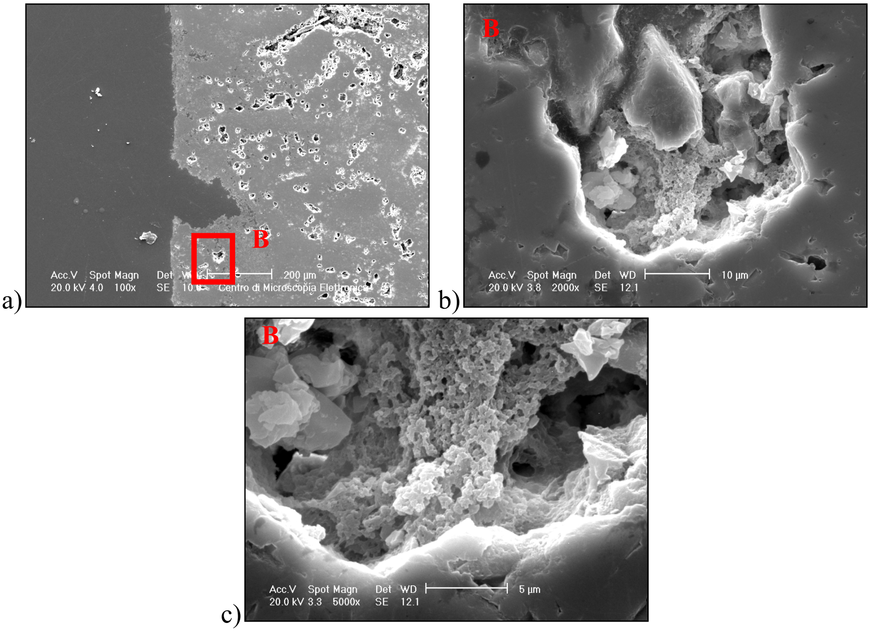

Figure 9: SEM micrographs on treated Poggio Picenze stone: a) sample section (scale bar 200µm); b)-c) different zoom views on **B** pore at about 300µm from the surface (scale bar 10 and 5µm, respectively).

In particular, in Fig.9b-c) internal stone cavities, that can be related to intergranular space, don't appear covered by the precipitated particles; this fact can indicate that the nanolime treatment doesn't modify the porosimetric system of the lithotype.

3.4 Pietra Serena stone

This lithotype is different from those discussed above; in fact, it is a sandstone characterised by clay fractions. Moreover, this stone is constituted by different grains size, ranging from medium-fine to coarse ones (Fig.10) [14].

SEM micrographs referred to the treated sample are shown in Fig.11; the internal voids appear filled, on the walls, by precipitated particles (shaped like a small "flakes") that tend to adhere to the clasts edges, without occluding the pores system (Fig.11b-c).

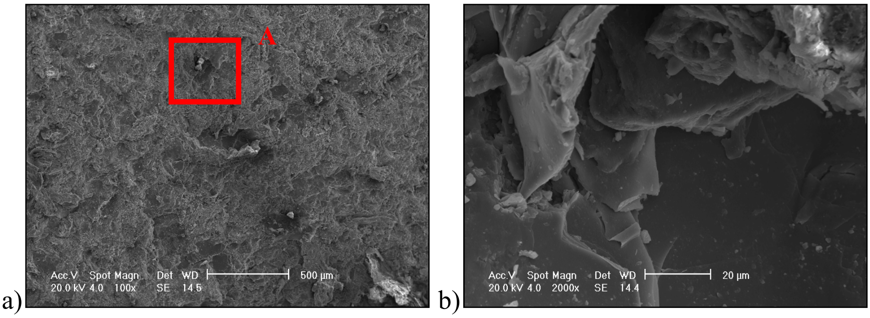

Figure 10: SEM micrographs on untreated Pietra Serena stone: a) sample section (scale bar 500μm); b) zoom view on **A** pore (scale bar 20μm).

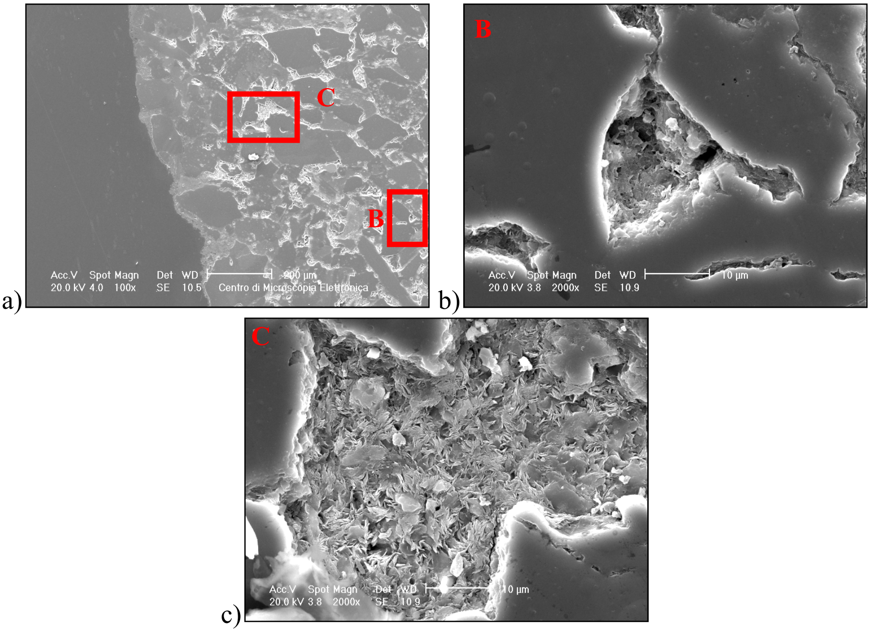

Figure 11: SEM micrographs on treated Pietra Serena stone: a) sample section (scale bar 200μm); b) zoom view on **B** pore localised at 750μm from the surface (scale bar 10μm); c) zoom view on **C** pore at about 450μm from the surface (scale bar 10μm).

3.5 Basalto stone

Basalt lithotype is an igneous rock lava of volcanic origin, typically composed by gray-black silicates [14]. It is an hard and resistant stone characterised by many pores and voids, of varying sizes, usually medium-large ones (Fig.12).

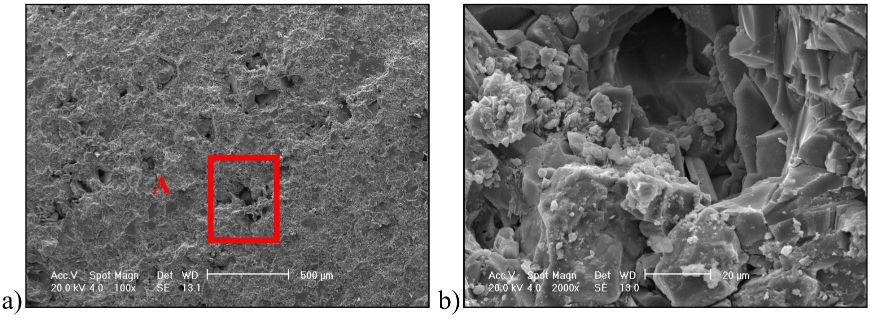

Figure 12: SEM micrographs on untreated Basalto stone: a) sample section (scale bar 500µm); b) zoom view on **A** pore (scale bar 20µm).

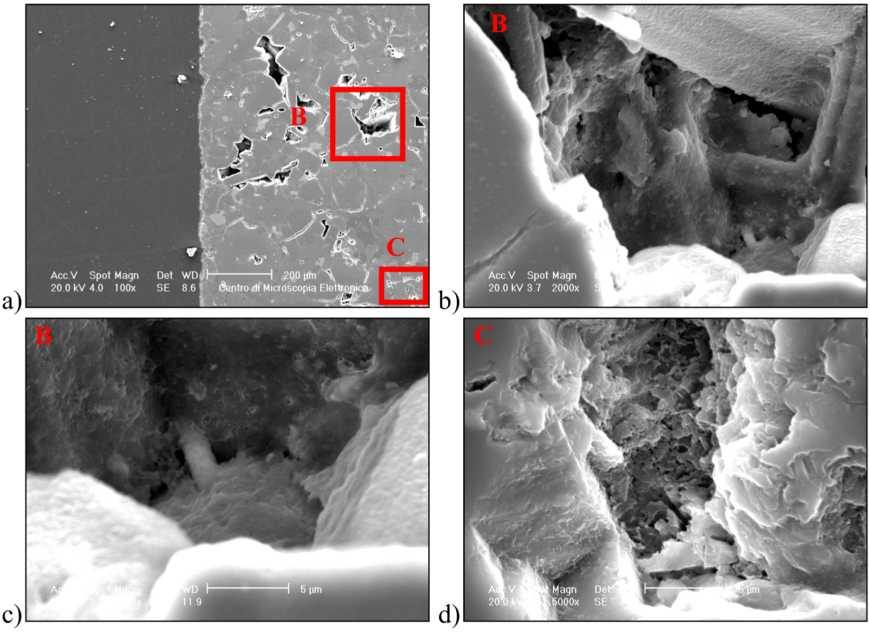

Figure 13: SEM micrographs on treated Basalto stone: a) sample section (scale bar 200µm); b)-c) different zoom views on **B** pore localised at 500µm from the surface (scale bar 10 and 5µm, respectively); d) zoom view on **C** pore at about 700µm from the surface (scale bar 5µm).

SEM micrographs on the treated stone, show as the nanolime treatment tends to fill the internal cavity of the material, adhering to its grain, without occluding the porosimetric system. In particular, the treatment, is not found in pores more internal than 700µm.

4 Conclusions

Nowadays lime nanoparticles are synthesised and employed for protection and superficial consolidation of several artworks such as stones, plasters, frescoes, wall paintings and paper documents.

The obtained $Ca(OH)_2$ nanoparticles are hexagonally plated and regularly shaped, with side dimensions generally less than 300nm, as shown by TEM observations. From XRD analyses, the carbonation process efficiency of the aqueous nanolime is about 50%, while the use of 2-propanol improves it reaching a *yield* value of about 80%. This result underlines the 2-propanol role in disagglomerating the particles, leaving a higher specific surface exposed to air. SEM analyses are performed to evaluate the interaction between the nanolime treatments and the porosimetric system of some natural lithotypes. The images show the partial filling of the pores in all the examined lithotypes, without occluding them. On the contrary, considering all the lithotypes, the treatment penetration is observed at a limit distance from the surface, ranging from 300µm (*Poggio Picenze* stone) to about 1mm (*Travertine* stone).

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