# THE MAYA SITE OF CALAKMUL: *IN SITU* PRESERVATION OF WALL PAINTINGS AND LIMESTONE USING NANOTECHNOLOGY

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ABSTRACT

Mexican cultural heritage, one of the richest in the world, is an essential source of iconographic and historical information about Mesoamerican civilizations. The influence of European schools of conservation is undeniable in the formation of Mexican conservation, which 'imported' most of the European conventional technologies, such as acrylic and vinyl polymers as organic consolidants, for the conservators of cultural heritage. Unfortunately, the unfavourable Mexican climate increased the rates of polymer degradation, and dramatic degradation effects, such as the severe flaking of surfaces and paint detachment, became apparent in a very short time. One possible conservation option used by some Mexican conservators was detachment of the paintings. A different approach, the subject of this contribution, is the use, instead of polymers, of physico-chemically compatible materials for conservation treatments, which ensure durable results. The paper highlights innovative methods based on nanotechnologies that have been tested for the *in situ* consolidation of paintings and limestone in *La Antigua Ciudad Maya de Calakmul* in Campeche, Mexico, designated a United Nations Educational, Scientific and Cultural Organisation (UNESCO) World Heritage Site since 2002.

ZUSAMMENFASSUNG

Das mexikanische Kulturerbe, eines der reichsten der Welt, ist eine essentielle Quelle zur Gewinnung von ikonographischen und historischen Informationen über mittelamerikanische Zivilisationen. Der Einfluss europäischer Konservierungstechnik auf die mexikanische Restaurierung ist nicht zu verleugnen, wie an dem Einsatz von Acryl- und Vinyl-Polymeren als organische Festigungsmittel für die Konservierung von kulturhistorischem Material deutlich wird. Unglücklicherweise führt das ungünstige mexikanische Klima zu einer Beschleunigung der Degradationsrate von Polymeren, weshalb dramatische Abbau-Effekte wie massives Abplatzen der Oberfläche und eine Ablösung der Malschicht schon in sehr kurzer Zeit sichtbar werden. Eine Möglichkeit der Konservierung, die von einigen mexikanischen Restauratoren durchgeführt wurde, ist die Ablösung der Malereien. Eine andere Herangehensweise, und Thema des vorliegenden Beitrages, ist die Verwendung physiko-chemisch kompatibler Materialien anstelle von organischen Konsolidierungsmitteln, womit beständige Ergebnisse erreicht werden können. In dieser Arbeit werden innovative, auf Nanotechnologien basierende Methoden für die *in situ* Konsolidierung von Malereien und des Kalksteins in *La Antigua Ciudad Maya de Calakmul* in Campeche, Mexiko vorgestellt, die seit 2002 zum United Nations Educational, Scientific and Cultural Organisation (UNESCO) Weltkulturerbe gehören.

## INTRODUCTION

Professional conservation in Mexico dates back to the 1960s. The influence of European schools of conservation, especially in the field of wall paintings, was fundamental for the development of early Mexican conservators, who used the traditional methods and materials employed for the restoration of European cultural heritage extensively for the conservation of pre-Columbian artefacts [1].

Unfortunately, some methods based on materials and recipes directly imported from Europe, produced devastating and completely unexpected degradation processes in Mexico's cultural heritage. Synthetic polymers, such as Paraloid B-72, Mowilith 30, and Primal AC 33, were mainly used during the 1970s and 1980s, with varied results. In controlled environments the results were often acceptable, for example, in colonial buildings. However, at several archaeological sites, the use of synthetic polymers to fix powdered and flaking paint (Palenque and Cacaxtla) and to re-adhere detached polychrome-modelled stucco fragments (Kohunlich) produced, after just a few years, dramatic effects on the artefacts, such as detachment and flaking of surfaces, and a strong acceleration of the chemical reactions involved in the paintings' degradation [1–4]. Polymers are unstable in most of the prevailing environmental conditions; drastic temperature and relative humidity changes, mechanical abrasion by dust and wind, rain and water condensation, light and pollution promote degradation. The final effect is the oxidation of polymer end-groups or side-groups, the chemical breakdown of polymer chain (chain-scission) and cross-linking reactions. All these processes lead to the loss of pigment adhesion, the yellowing of polymers, a decrease in polymer solubility and the treatment becoming irreversible.

These side-effects induced conservators to search for new materials and conservation methods and to revise the protocols used for restoration. The environmental conditions of some regions of Mexico, very different to those found in Europe, forced local conservators to modify European methods in order to find restoration procedures appropriate to the materials used for Mexican artefacts and to the different climate. For example, the warm subtropical climate of Yucatan has a mean annual temperature of 27°C and a low of 18°C, with a mean annual precipitation of 750 mm, all of which imply high relative humidity. These severe climatic conditions accelerated the degradation processes of polymers, making the effect of degradation obvious in a relatively short time. European paintings treated with polymers share the same fate, but they are following a slower degradation curve. These severe side-effects discouraged most Mexican conservators from using polymers for consolidation or fixation of wall paintings [5–7] and they reverted to the large-scale use of lime-water [1, 8].

Correct restoration practice recommends that inorganic materials, such as wall paintings, stuccoes, and limestone, should be restored only using inorganic methods and, when possible, by reversing the chemical reactions leading to the degradation of the artefacts [9–11]. Restoration should be as reversible as possible, and the materials applied to the works of arts must be as compatible as possible, and possibly the same, as those used in the artefacts.

Restorers often remove materials in the form of fat, salts, varnishes and pollutants from the surfaces by using chemical and mechanical methods, which may also affect the substrate; therefore, every restoration treatment should be considered as invasive [12]. For example, the materials used for consolidation and protection can penetrate the porous structure of the work of art, markedly modifying the original characteristics of the object and making it hard to predict the lifespan of the restored materials [13]. Only in the last few years have criteria for treatment, such as compatibility, minimal intervention or reversibility, found some practical applications with the emergence of new techniques based on nanotechnologies [9, 14–19]. Some innovative inorganic methods based on nanotechnologies have provided new methods for the consolidation of paintings [16, 17]. In particular, by using these compatible methods, it is possible to perform interventions *in situ* without modification of the physico-chemical and mechanical behaviour of the materials, ensuring long-lasting effects without any detachment needed to preserve the works of art.

### *The Maya archaeological site of Calakmul*

*La Antigua Ciudad Maya de Calakmul* is located in the region of Peten in the southern part of the state of Campeche, close to the border with Guatemala [20, 21]. The city is deep in the

Calakmul Biosphere Reserve, a protected area of more than 724000 hectares of tropical jungle that keeps many endangered species of fauna and flora protected from collection and hunting.

Calakmul, along with Tikal in Guatemala, is the most important city from the Classic Maya period (AD 250–800) owing to the great number of sculpted monuments that record the history of the lineages inhabiting the site (more than 120 stelae are reported), the size and complexity of the structures, and the architectural and artistic manifestations produced throughout its occupation expressed in ceramics, mural painting and funerary rituals, among other elements. There is archaeological evidence that indicates the city was inhabited for more than 12 centuries, starting around 400 BC (Pre-Classic period) and then was slowly abandoned towards the year AD 900 (Post-Classic period), reaching the height of its development in AD 600–800 (Late Classic period).

Calakmul was discovered by the botanist Cyrus Lundell in 1931, who gave the archaeological site the present name that in Maya language means *Ca* 'two', *lak* 'close', *mul* 'artificial hills or mounds'. The urban area of Calakmul occupies a natural dome covering around 25 $km^2$, surrounded by a lower area, or *bajo*, that collects water during rainy seasons. Fundamentally, the city is distributed in six main areas: *Gran Plaza, Gran Acrópolis, Acrópolis Norte or Acrópolis Chik Naab, Grupo Noreste, Grupo Suroeste* and *Pequeña Acrópolis.* Around 6250 features have been surveyed, including buildings, sculptures, monuments such as stelae, and altars, spread throughout the city. Figure 1 shows a map of Calakmul's nucleus.

*The Proyecto Arqueólogico Calakmul*

The *Proyecto Arqueólogico Calakmul* was established in 1993 with the support of the government of the state of Campeche, the Instituto Nacional de Antropología e Historia (INAH) and the Secretaría de Turismo and Secretaría de Desarollo Social, among others. This project, directed by the archaeologist Ramón Carrasco Vargas, brings together several institutional partners, including the Universidad Nacional Autonoma de Mexico — UNAM and the University of Florence (CSGI, the Italian Centre for Nanotechnologies), and involves the collaboration of archaeologists, restorers, physical anthropologists, architects, engineers, chemists and epigraphists, among other specialists.

From 1993 to 2005, excavations of the whole site have been planned and carried out year after year. Exploration and restoration of the *Gran Plaza*, *Gran Acrópolis* and the *Acrópolis Norte* or *Acrópolis Chik Naab* were undertaken between February and September 2005. The objective of these studies was to obtain additional data leading to a better understanding of the different construction and occupational sequences of the structures on site. Work was concentrated in Group A and Structure I of the *Acrópolis Chik Naab*, where well-preserved wall paintings from the Early Classic period (250–600 BC) were further researched and are presently being restored. Additional work was also performed for the Late Pre-Classic (400 BC) great polychrome-modelled stucco mask, which measures approximately 375 × 170 cm and is located in the *Gran Plaza*, Structure II, substructure II-c1, Figs 1–3 [22].

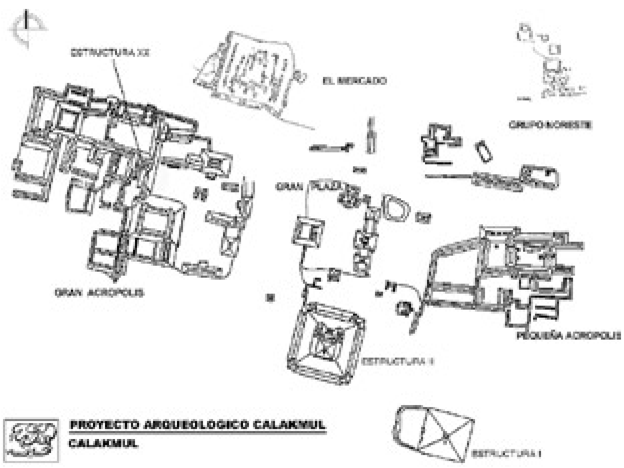


Fig. 1 Map of the ruins of Calakmul. Courtesy of Proyecto Arqueologico Calakmul.

Fig. 2 Aerial view of Structure II.

Fig. 3 Polychrome-modelled stucco mask in the sub-structure II c-1, in the inner part of structure II. The image was taken after readhesion of several detached fragments using autogenously air-setting mortar.

The mural and great mask were identified during the exploration for earlier structures and were found to have been intentionally entombed using a select set of materials and a thick layer of fill, consisting of decomposed stucco mortar and plaster and limestone, followed by later building sequences. The deliberate and careful burial of these features indicates an intention to preserve them, possibly for some religious reason [23].

In *Acrópolis Chik Naab*, the Group A murals were located on the backrest and lower part of a bench-like feature that served as a 'walkway' and boundary between this Acrópolis and the central area of the city. In Structure I of the same Acrópolis, mural paintings were found covering the walls of the pyramidal substructure. This structure is dated to the Early Classic Period, with a 10.3 $m^2$ base and a height of 4.8 m.

From these recently discovered paintings the first group (Group A) was found partially preserved. The east and west sections of Structure I have been explored, with the east section found to be very well preserved and the west section partially preserved. It is important to note that the exploration and restoration process is still in progress and there are high expectations of finding additional well-preserved paintings.

The mask from substructure II-c1 was found to have been part of the building's façade, flanking the main stairway that provided access from the *Gran Plaza* level to the inner part of the architectural compound that is behind, to the south. Another mask has been identified in the west part of the building's façade; it is expected that two additional masks will be found on the lower part of this façade. The general condition of the polychrome-modelled stucco mask found during the exploration process was good: some sections had separated from the support and, in some cases, cracked, but had remained *in situ*. The pigments decorating the modelled stucco were found to be in a good state of preservation. The exposure of these features to new environmental conditions (light, temperature and humidity) was monitored and controlled to minimize potentially adverse effects. This was achieved by the installation of covers, and limiting the presence of individuals to the minimum number necessary to perform the delicate excavation and restoration work.

Learning from previous conservation treatments based on the use of organic materials, it was decided to take a different approach for treatment. For example, in the archaeological site of Kohunlich, the severe damage displayed by the modelled stucco polychrome masks treated with synthetic polymers was the result of the polymers' degradation due to exposure to a tropical climate, with a progressive disintegration and detachment of fragments [4]. Conservation treatment was carried out from 1969 until the present using Paraloid B-72, ethyl silicate and a grout of lime mixed with calcium casein applied by immersion, injection, and surface impregnation. Synthetic polymers confer impermeable characteristics to the material treated, while stucco is quite permeable to water and water vapour. This treatment therefore inhibits transpiration and moisture from flowing through the porous structure of the stucco and leads to salt crystallization beneath the polymer layer applied to the surface, with associated strong mechanical stress caused by the growth of salt crystals. At present the masks show loss of cohesion, salts micro-organisms and a surface coating with a 'plastic' appearance. Precise data regarding the effect of organic consolidants on stucco and wall paintings in warm sub-tropical climatic conditions are now available [5, 6]. Considering that the Biosphere of Calakmul has similar characteristics to that of Kohunlich, a different approach for the conservation of stucco and paint has been taken, as described below.

## AUTOGENOUSLY AIR-SETTING MORTARS FOR CONSOLIDATION

Mural painting and decorative stuccoes are layered structures. A common consequence of this is that separation between layers easily occurs. Variations in temperature, relative humidity and other factors produce mechanical and physical stress that can be responsible for the complete or partial flaking or detachment of these layers. Sedimentary limestone very often shows similar degradation, in the form of cracks and delaminations. Several materials have been used to re-adhere delaminating layers and/or to fill voids in degraded limestone: hydraulic grouts (Portland cement), plaster of Paris and organic binders mixed with or without filler. The physico-chemical properties of these materials are different from those of the lime-based mortars and limestone and produce local variations and heterogeneity in the wall painting or stone structure. In the long term these promote fractures, cracks and loss of cohesion; in a word, degradation. A grouting with the same composition as the original material is preferable for conservation treatment, since the newly-introduced materials should be, in principle, compatible with the wall paintings and/or limestone.

Lime-based adhesives have the same physico-chemical properties as wall painting and stuccoes, but they require $CO_2$ to set. Unfortunately, the $CO_2$ uptake into a porous structure is too slow and inefficient for setting; therefore, a possible solution is the use of lime-based grouts with an additive that slowly produces carbon dioxide. A number of possible solutions have been investigated during the years:

- Water saturated with $CO_2$ (unsuccessful since the high solubility of $CO_2$ in water lowers the pH and the acidic solution quickly reacts with $Ca(OH)_2$).
- Autogenous $CO_2$ production from additives.

Additives producing $CO_2$ by reaction with water in an alkaline environment have been identified in the group of carbonic acid esters, and tested for wall paintings consolidation. These compounds are carbamates, with the general formula $R\text{-}O\text{-}CO\text{-}NR'_2$, where $R=C_2H_5$ and $R'=H$ in ethyl carbamate (EC). Ethyl carbamate was successfully used for consolidation through injection of frescoes by Masaccio, Lippi and Masolino in the Brancacci chapel in Florence, Italy [24].

Mortars containing carbamates were called 'autogenous mortars', since the setting process occurs without involving $CO_2$ from the atmosphere. The alkaline hydrolysis of these compounds is represented by the following reaction [25]:

$$C_2H_5\text{-}O\text{-}CO\text{-}NH_2 + H_2O \rightarrow C_2H_5OH + CO_2 + NH_3$$

Carbon dioxide is produced *in situ,* and all the other decomposition products are released, without damage to the work of art. The reaction is not particularly fast in a basic environment, and takes more than a month to complete. In a previous publication, encouraging preliminary results showed that ammonium carbamate was a very efficient $CO_2$ autogenic additive, in addition providing an ideal fluidity to the mortars [24]. This paper reported the main findings of the studies on ammonium carbamate ($R=NH_4^+$, $R'=H$), which produces ammonia and carbon dioxide by decomposition. The correct amount of the additive has been determined, and a comparative study of mortars with different composition has been carried out in order to describe the kinetics of the carbamate hydrolysis and the subsequent mortar setting process (dehydration *plus* carbonation).

The setting process involves several stages, the most important being the formation of calcium carbonate nuclei and their growth until they overlap to form a continuous structure. This process can be satisfactorily described by the Avrami-Erofeev kinetic mechanism that accounts for a solid-state reaction with nuclei formation, where nuclei growth is controlled by diffusion of the reactant at its interface [26].

Mortars with ammonium carbamate have been used for repairing detached stucco fragments and also for filling voids and re-adhering flaking layers. This paper specifically reports their use on the polychrome-modelled stucco mask in sub-structure II c-1 in the inner part of structure II, Fig. 3. In this case, the mortar was used for the re-adhesion of large pieces, Fig. 4. The degree of carbonation of the mortar used for the intervention was investigated by X-ray diffractometry (XRD) on reference material. Experiments showed that carbonation of autogenously air-setting mortar initiates a high-binding calcite capacity, while $CO_2$ from the air does not ensure a fast and efficient carbonation of the mortar, Fig. 5. A detailed description of the laboratory tests is reported in Appendix 1. The procedure for the application of autogenic mortars does not require any specific technical skill, and the costs for the preparation of mortar are modest, or lower than those of the materials commonly used for restoration (Appendix 1).

## NANOPARTICLE DISPERSIONS FOR THE CONSOLIDATION OF WALL PAINTINGS

Although wall paintings can be very stable over a long period of time, they sometimes develop serious deterioration phenomena. This is mainly due to the action of water and solutions of salts/pollutants soaking the porous matrix of the wall. Natural ageing instigates flaking of the paint layer and powdering of the painted surface, due to corrosion of the binding calcium carbonate, with


Fig. 4 Polychrome-modelled stucco in sub-structure II C-1 of the Gran Plaza: (a) before restoration; (b) post-restoration. Re-adhesion of detached fragments was performed using an autogenously air-setting mortar.

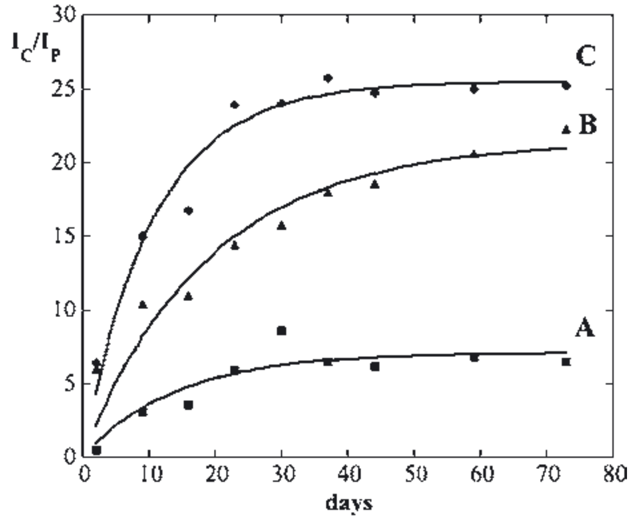


Fig. 5 Degree of carbonation of lime plus quartz plaster measured by intensity peak ratio (calcite vs portlandite). Curve A: mortar setting in a $CO_2$-free environment without additive; curve B: mortar setting in a $CO_2$-free environment with $CO_2$-producing additive; curve C: reference mortar setting in air.

a loss of cohesion between pigments and substrate. Therefore, the whole physico-chemical compatibility between the original materials and the restoration products can only be completely achieved by using calcium hydroxide ($Ca(OH)_2$). This is the best remedy for wall painting reinforcement, since $Ca(OH)_2$ is the 'original' binder used by the artists.

Lime-water can be used, but its efficacy is limited by the poor solubility of calcium hydroxide in water (1.6 $g.L^{-1}$). Aqueous suspensions of commercially-available $Ca(OH)_2$ cannot be used, since the sedimentation rate is too fast and the particle size is too large, often producing white glazing over painted surfaces. The particles have a broad size distribution and the mean size is in excess of several micrometers. Dispersions of nanosized particles in non-aqueous solvents produce kinetically-stable systems, and can solve most of the drawbacks mentioned above [15–17].

Stable nanodispersions of calcium hydroxide have been successfully applied as fixatives to re-adhere lifted paint layers during many restoration programmes in Italy and elsewhere in Europe, and as a consolidant. The application of nanoparticles is equivalent to the application of an extremely concentrated solution of lime-water, but nanoparticles are well above the physico-chemical limit imposed by the solubility of calcium hydroxide in water. A detailed description of the synthesis and of the application procedure is reported in Appendix 2.

Decorative glyphs, painted over stucco plaster at the base of the columns, recovered in Structure XX (the *Gran Acrópolis*) of Calakmul had a friable and powdered paint layer, which needed consolidation. The consolidation was performed using nanoparticle dispersions applied by gentle brushing, Fig. 6a. Following the application of nanoparticles, a wood-fibre poultice soaked with water was applied for eight hours in order to keep the upper paint layers wet, Fig. 6b. A few days later, a second application of nanoparticles was made. At the end of the whole treatment, a simple test with a wet cotton-wool swab demonstrated that the colour was now completely fixed, Figs 6c–d.

Nanoparticle dispersions were also used in Early Classic period wall paintings of the *Acrópolis Chik Naab*. Fig. 7 shows some steps in the excavation and an overview of the whole painting, which had several areas with powdering paint surfaces, where dispersions were used to fix the colours and to consolidate the painted layer.





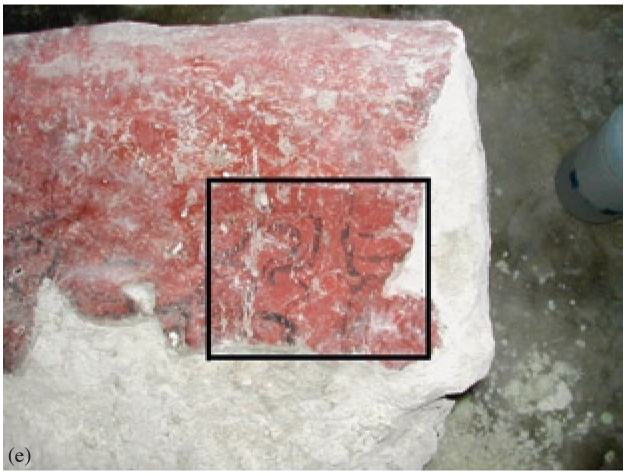


Fig. 6 (a) Application, by brushing, of nanoparticle dispersion on decorative glyphs; (b) wood-fibre poultice soaked with water applied for eight hours in order to keep the first paint layers wet; (c) powdered pigments removed with a wet cotton-wool swab before fixing of paint layer; (d) test repeated on the consolidated area (indicated by the box in Fig. 6e); (e) the paint layers a few days after the completion of the treatment.


Fig. 7 (a)–(b) Discovery and excavation of wall paintings of Structure I in the *Acrópolis Chik Naab*; (c) overview of the paint after consolidation treatment with nanoparticles.

The level of degradation of the paintings did not allow the extensive use of water, since the paint layers were in most cases very friable and weak. The use of alcohols as carriers for nanoparticles avoided possibly dangerous consequences of the restoration through the solubilization of salts in the painted layer. Furthermore, nanomaterials are characterized by a high surface area that influences the chemical reactivity of nanoparticles, producing a consistent consolidation of treated surfaces just a few days after application. These positive effects can be particularly important on archaeological sites where *in situ* conservation requires effective conservation and preservation treatments.

## CONCLUSION

*In situ* conservation is a challenge for archaeologists and restorers. Often, due to the harsh environmental conditions, works of art are subjected to severe deterioration processes. To avoid this, several wall paintings have been detached in the past and moved to a controlled environment indoors. Attempts to protect paint by using synthetic polymers produced even worse effects, so that the conservation of cultural heritage in the original context where it was created still remains an ambitious task.

Innovative methods based on nanotechnologies, one of the most popular topics in pure and applied science, might offer new ways to treat inorganic supports, such as stone, stucco and wall paintings, with long-lasting effects. Nanoparticles ensure a high physico-chemical compatibility that gives long-term stability and protection. Nanoparticle technology was applied to the conservation of stucco and paint in the archaeological site of Calakmul with extremely good results. The experiments performed in Calakmul will be monitored for two years, in order to define the best procedures to be used in the larger area where archaeological sites share the same materials, techniques and environmental conditions.

## APPENDIX 1

*Autogenously air-setting mortar: application procedure and laboratory tests*

The analysis performed by calcimetry and XRD of mortar samples from Calakmul guided the formulation of grout mixtures to match the chemical composition of the original artefacts that were to be preserved. A grout mixture for application *in situ,* was made with 1:1 (volume to volume) lime and fine limestone powders (size around 30–50 $\mu$m, 325 mesh) obtained from the stones present in Calakmul; around 3% w/w ammonium carbamate was used to encourage carbonation.

Early on, some mortar samples were prepared by mixing slaked lime with inert materials. Different mortars prepared by mixing the binder with quartz, kaolin, and limestone powders (to obtain a paste simulating those used in Calakmul) in a volume ratio 1:1, plus de-mineralized water, were investigated. The plasters were put into a wood mould (dimensions 50 × 50 × 10 mm) on a brick support. In order to achieve carbonation in a $CO_2$-free environment, samples were placed in a dry-box under nitrogen. Reference mortars with no additives were left to set in the air.

The degree of carbonation was investigated by XRD, using a D8 advance (Bruker AXS) diffractometer equipped with a Cu $K_\alpha$ tube, and carried out on powdered samples between 15 and 85º as 2θ values and by calcimetry according to the Dietrich-Frühling method. Fig. 5 shows the carbonation behaviour of the plaster. The curve labelled A refers to a sample kept in a $CO_2$-free environment without any $CO_2$-producing additive; curve B refers to a sample with an additive, and curve C refers to a sample allowed to set in contact with air. The graphs report the intensity ratios between the signal for calcite (29.6°, I=100) and portlandite (28.7°, I=74). The comparison of the curves clearly shows that carbonation of autogenously air-setting mortar took place, reaching a high-binding calcite content. The setting of mortar with carbamate had not reached the asymptote after 70 days and it is still in progress, Fig. 5. Complete setting can be estimated to be achieved in six months to one year.

## APPENDIX 2

*Synthesis and purification of nanoparticles from a homogeneous phase reaction*

Calcium hydroxide nanoparticles were obtained by mixing a 0.2M NaOH solution with a 0.1M $CaCl_2$ solution, both at 90°C. A calcium chloride solution was stirred with an ultraturrax disperser (IKA, Stauffen, Germany), which behaved as a mechanical grinding device working at 5000 rpm. Sodium hydroxide solution was added by a syringe close to the top of the disperser, so that the solution entered into the vortex generated by the ultraturrax and nucleation of the calcium hydroxide occurred at the same time as grinding. This greatly reduces the growth of newly-formed crystals, limiting the size of particles. An aqueous suspension of $Ca(OH)_2$ was gradually cooled down to room temperature in a nitrogen atmosphere to avoid $Ca(OH)_2$ carbonation.

Nanoparticles have been purified from co-precipitated NaCl through dialysis. This consisted of a tubular membrane into which dispersions of freshly-prepared particles were placed. Tubes were left in a beaker with ultra-pure water for at least 72 hours, changing the water every 18 hours, until no chloride ions were detected by an $AgNO_3$ solution test. Finally, particles were collected by filtering through a 0.1 μm Millipore membrane.

Nanoparticles have been re-dispersed by mixing 10 g of calcium hydroxide paste with 1 L of alcohol, under vigorous agitation. Very stable dispersions of nanoparticles can be obtained in alcohols (mainly 1- and 2-propanol). The features of these solvents (volatile, low toxicity, low surface tension and with a density and viscosity similar to water) make the application methodology very simple and manageable, i.e. brushing and spraying. Calcium hydroxide nanoparticles have been applied in Calakmul by brushing, after protecting the painted surface with sheets of Japanese tissue paper.

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## MATERIALS AND SUPPLIERS

Sodium hydroxide, NaOH, calcium chloride dihydrate, $CaCl_2.2H_2O$, quartz, $SiO_2$ (40–100 mesh; purity > 99.0%) and ammonium carbamate: Merck, Frankfurter Str. 250, 64293 Darmstadt, Germany.

Cellulose membranes for dialysis: Sigma-Aldrich, http://www.sigmaaldrich.com.

The water used was HPLC-grade (resistance > 18 MΩ.cm), obtained by a Milli-RO6 plus Milli-Q-Water System: Millipore, Millipore Corporate Headquarters, 290 Concord Road, Billerica, MA 01821, USA.

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