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2nd INTERNATIONAL CONSERVATION SYMPOSIUM-WORKSHOP

Natural History Collections

6 - 9 May 2015 BARCELONA - SPAIN

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PREFACE

This special volume collects the work of some of the attendees and the international guests to the 2nd International Conservation Symposium-Workshop in Natural History Collections, organized by the CRIP (Centre of Paleontological Restoration and Interpretation) of Els Hostalets of Pierola, Barcelona (Spain), together with the Museum of Natural History of the Smithsonian Institution of Washington (USA), the National Museums of Scotland in Edinburg (UK) and the Natural History Museum of London (UK).

This international symposium aimed to create a workspace and study around the concepts of protection and conservation of Natural History Collections, deepening the knowledge and analysis of the different working methods used in this type of collections. Participation in the symposium was a great success with over 60 participants from different parts of the world: Norway, Denmark, Sweden, Israel, England, Portugal, USA and Spain.

This second international meeting was a great space for discussion and exchange of experiences, very dynamic and profitable, where professionals from around the world debated and reflected around the conservation, preparation and restoration of Natural History Collections, establishing ties of professional and institutional collaborations among the participants. The symposium organizing committee wishes to thank all participants and collaborating institutions whose participation has made this meeting possible. And also we want to thank the Journal of Paleontological Techniques for the realization of the Symposium Volume. The team of the Journal of Paleontological Techniques put a lot of effort in editing and publishing this volume monograph.

Organizing committee

Sandra Val – Rubén García – Steve Jabo – Vicen Carrió

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FOSSIL TRACKS AND TRACKWAYS: THE DILEMMAS OF PRESERVATION

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ABSTRACT

Important fossil bones are generally excavated and removed from a site. There are exceptions as when *in situ* displays are possible or preferred because of the extent of the fossil field or the large number of the same species does not justify removal. Fossil bones typically have a three-dimensional physicality that allows their excavation and transportation, whereas fossil tracks are mere impressions in the substrate, and most trackways are not removed. Tracks are vulnerable to damage and loss, generally more so than bones, so that removal may place them at risk and at the same time it destroys the context of the tracks in their landscape setting, which in some instances affects the significance, even though recording has been done, as at the Laetoli hominid trackway site in Tanzania. Other options for preservation in situ, are sheltering and reburial. This paper discusses the options and a number of examples of in situ preservation efforts for track sites and fossil bone sites to illustrate the issues. The examples reveal that there is no panacea and the conundrum of how best to preserve yet make accessible the evidence of fossil sites is difficult to solve. When non-scientific intangible values such as symbolic significance, exemplified by the fragile Laetoli tracks, are taken into account preservation requirements for the site in its setting preclude removal and preservation options are limited to reburial or sheltering. Each of these has drawbacks. Only a rigorous assessment of the sites condition, threats and management context will result in a solution that has the greatest likelihood of success.

Keywords: preservation; conservation; tracks; trackways; hominids

RESUMO [in Portuguese]

Ossos fósseis importantes são geralmente escavados ou removidos de uma jazida. Há algumas excepções, como quando exposições *in situ* são possíveis ou preferíveis porque a extensão da jazida ou o elevado número da mesma espécie não justifica a sua remoção. Ossos fósseis tipicamente possuem uma tridimensionalidade que permite a sua escavação e transporte, enquanto pegadas fósseis são meras impressões no substrato, e a maioria dos trilhos não é removida. As pegadas são susceptíveis de dano ou perda, geralmente ainda mais do que ossos, tornando a sua remoção arriscada e ao mesmo tempo destruindo o contexto das pegadas no seu enquadramento, o que, em alguns casos, afecta a sua significância, mesmo que haja um registo feito, como por exemplo no trilho de hominídeos de Laetoli, na Tanzânia. Outras opções para preservação in situ são abrigar a jazida ou o enterramento. Este artigo discute as opções e alguns exemplos de esforços de preservação in situ de jazidas de pegadas e ossos fósseis de forma a ilustrar os problemas. Os exemplos revelam que não existe uma panaceia e que o enigma de como melhor preservar, mas mantendo acessíveis l as jazidas fósseis, é difícil de resolver. Quando valores intangíveis não científicos, como significado simbólico, exemplificado pelas frágeis pegadas de Laetoli, são tidos em conta, os requisitos de preservação para a jazida no seu enquadramento impedem a remoção e as opções de preservação são limitadas a enterramento ou à construção de abrigos. Cada um destes tem desvantagens. Apenas uma avaliação rigorosa das condições das jazidas, ameaças e gestão resultarão numa solução com a maior probabilidade de sucesso.

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INTRODUCTION

Fossils, whether tracks, traces or bones, are the subject of scientific enquiry by paleontologists and are also of enduring interest to the public. The wealth of information, as it were a window into the deepest past of the origin and evolution of life on the planet, is what the fossil record offers. This is the usual perception of the value of fossil material – a way in which the methods of science can elucidate, date and understand evolutionary trees and extinctions over time. Fossils, however, may also touch a deeper chord in society. Discoveries about the origin of the human species, for example, are almost guaranteed to make headline news and catapult the discoverer into the realm of the famous. The subject is an abiding interest of society today and as such fossil material relating to our origin has cultural as well as scientific value. Human origins is one of the few areas where science and the humanities truly merge and where the methods of science evoke wonder and reflection and allow us to view the place of our species in a humbler context among the spectrum of life, particularly vertebrate life, and specifically as a member of the primate family. Vying for, or often exceeding, interest in human origins are the dinosaurs, whose fossil bones and tracks share issues of conservation with those of hominin footprints.

The preservation of fossil material can be challenging, especially when left in situ. Bones are typically excavated and removed from the site for preservation in laboratory and storage or display in museums. There are, however, instances when in situ display is possible without apparent deterioration - the exception rather than the rule – as when the extent of the fossil field or the sheer number of the same species makes removal of all but a few both too costly and unnecessary. Such is the case of Dinosaur National Monument in Utah that has a famous display in a protective shelter, the "Wall of Bones" with approximately 1500 fossils embedded in the cliff face (http://www.nps.gov/dino/planyourvisit/quarry-exhibit-hall.htm). A very different example is Wadi el Hitan World Heritage Site in the Fayoum area, south of Cairo, where fossil remains of the earliest, and now extinct, suborder of whales, Archaeoceti, are exposed at the surface over a large area. Some of the fossils are casts reproduced as originally found, others are authentic fossils. All are part of a national park with creative interpretive shelters and panels and may be visited on foot in a beautiful desert environment (Figure 1). While the management of the site appeared exemplary during early years of opening in the mid-2000s, this type of open display is extremely vulnerable to erosion from wind and physical damage or pilfering if management

Figure 1 - Wadi el Hitan fossil whale ancestor site in the Fayoum area of Egypt is an open-air fossil park in a desert environment.

Figure 2 - The fossils of Wadi el Hitan, originals and replicas, remain in situ with interpretation and minimal barriers, providing a good visitor experience, but leaving them vulnerable to vandalism and erosion.

systems break down (Figure 2). In other instances, although unusual ones, removal of fossil specimens has resulted in later loss, as in the famous Peking Man specimens from China that disappeared during World War II (Boaz and Ciochon, 2004; China Heritage Project, 2005). Nonetheless, fossil bones have a three-dimensional physicality that allows their excavation and transportation, whereas tracks are mere impressions in the substrate and their conservation in situ is more complex.

Tracks and trackways

Fossil tracks and trackway sites are common around the world. This is not surprising because a vertebrate animal moves while living and leaves many traces but once it dies it leaves only one set of remains. Tracks record a moment in time, recent or many millions of years ago, and evoke speculation about the track maker and the circumstances under which the tracks were made. Furthermore, tracks and trackways often provide information that bones cannot: behavior, stride, soft tissue morphology, and claw marks, for example. Invariably imprinted in sediments, tracks however can be highly susceptible to loss. From a preservation point of view it is not relevant to distinguish between categories of track maker. What is important is scientific and cultural value assigned to a particular site; its physical condition and threats; and the management context in which it will be preserved.

The impression of animal tissue in the substrate carries the information and it is the impression that is the objective of preservation. Tracks are found in many sedimentary substrate types from mud to sandstone to volcanic ash fall. At the time of impression all were soft and had enough cohesion to take and retain the impression. Usually the substrate was damp enough for this to happen. Later through natural burial, or protection from weathering as in caves, the impression survived or was transformed through lithification into more durable rock types such as sandstone, shale, or tuff in the case of volcanic deposits. Unquestionably a great many more tracks and trackway sites were lost to natural erosional processes than have survived, and the continuing frequency of discovery of new sites indicates that there are many yet to be discovered when we train our eyes to see them.

PRESERVATION OPTIONS

The conundrum of how best to preserve these vulnerable traces, yet make accessible the evidence of fossil tracks, is difficult to solve and in many instances there are no good options, just less bad ones. Any search for the best preservation solution, however, must begin with a rigorous assessment of in situ versus ex situ options and a clear recognition of the obstacles to sustainability. Three principal preservation options have long been practiced:

Ex situ preservation: Museum storage

Because of their unique characteristics, when tracks or trackways are found scientists may argue for their removal to a museum. Intrinsically, there is no doubt that museum storage of removed fossils, whether tracks or bones, away from the hazards of the outdoor environment offers better protection, but not necessarily always, especially in developing country contexts. Humid conditions in museums, for example, may in fact accelerate decay as with framboidal pyritic fossils that oxidize, liberating sulfur oxides and sulfuric acid to the detriment of other museum objects stored in proximity to the affected fossils (Howie, 1979). Egyptian material in the British Museum containing both hygroscopic salts and smectite clays have been documented to undergo quite drastic deterioration in comparatively short time periods in unsuitable humid storage (Bradley and Middleton, 1988; Rodriguez-Navarro et al., 1998). More to the point in terms of removal of tracks for their protection is the example of the Cretaceous tracks from Dinosaur Valley State park along the Paluxy River near Glen Rose, Texas, which were lifted out in parts and moved to the Texas Memorial Museum, where they have survived well, and to a purpose built display structure, where the in situ tracks suffered severe deterioration (Shelton et al., 1993), and the example of the Langebaan Holocene footprints from South Africa, which suffered loss when being removed to a museum (Roberts, 2008). Thus, removal to museum storage is by no means the panacea it may seem to be. Moreover, museum storage facilities are often overcrowded and poorly maintained in regions where inadequate resources are available for good curation of collections, and objects may be forgotten, inaccessible, in effect lost. Last, but sometimes most importantly, removal of tracks destroys the context and thereby diminishes both cultural and scientific value. Thus in situations where removal is the only option, the necessity of comprehensive documentation becomes paramount.

In situ preservation: protection by sheltering

The option of in situ conservation without the protection of a shelter cannot be considered a preservation option, although many track sites that are extensively excavated or exposed through natural erosion may be so treated. Such is the case of the 120,000 years old human footprints in volcanic ash from the very remote site of Engaro Sera near Lake Natron in northern Tanzania. These were exposed mainly through erosion of the thin top soil and have remained exposed (Figure 3), ensuring their demise if nothing is done to protect them. Keeping a site in situ under the protective cover of a shelter is a commonly espoused and implemented response to the problem of conserving archaeological sites, in which category we include track sites. There are thousands of shelters over archaeological sites worldwide and this option is especially favored for visited sites or on sites that hope to attract visitors. Unfortunately it is one that frequently results in little or no benefit to the site and sometimes leads to further deterioration. The reasons are many, but there are two principal ones: 1) the difficulty of understanding and then re-creating through design of a shelter an environment that will provide long-term stability for the archaeological remains being covered; and 2) lack of sufficient or proper maintenance of the shelter and/or site over time. A common approach to sheltering – 'build it and they will come' – assumes a naïve understanding of tourism, its costs and its impact on sites and local communities. In fact, while ostensibly shelters are built to protect sites, they are primarily erected when there is the expectation that the site will be visited. When few visitors come, in due course the funds for maintenance, staffing and operations dry up. In the long run neglect and deterioration are often the result: hence, the importance of a realistic assessment of the management context in which the site must survive. For a comprehensive review of the issues and an annotated bibliography on shelters over archaeological sites see Stanley-Price and Matero (2001) and Demas (2013).

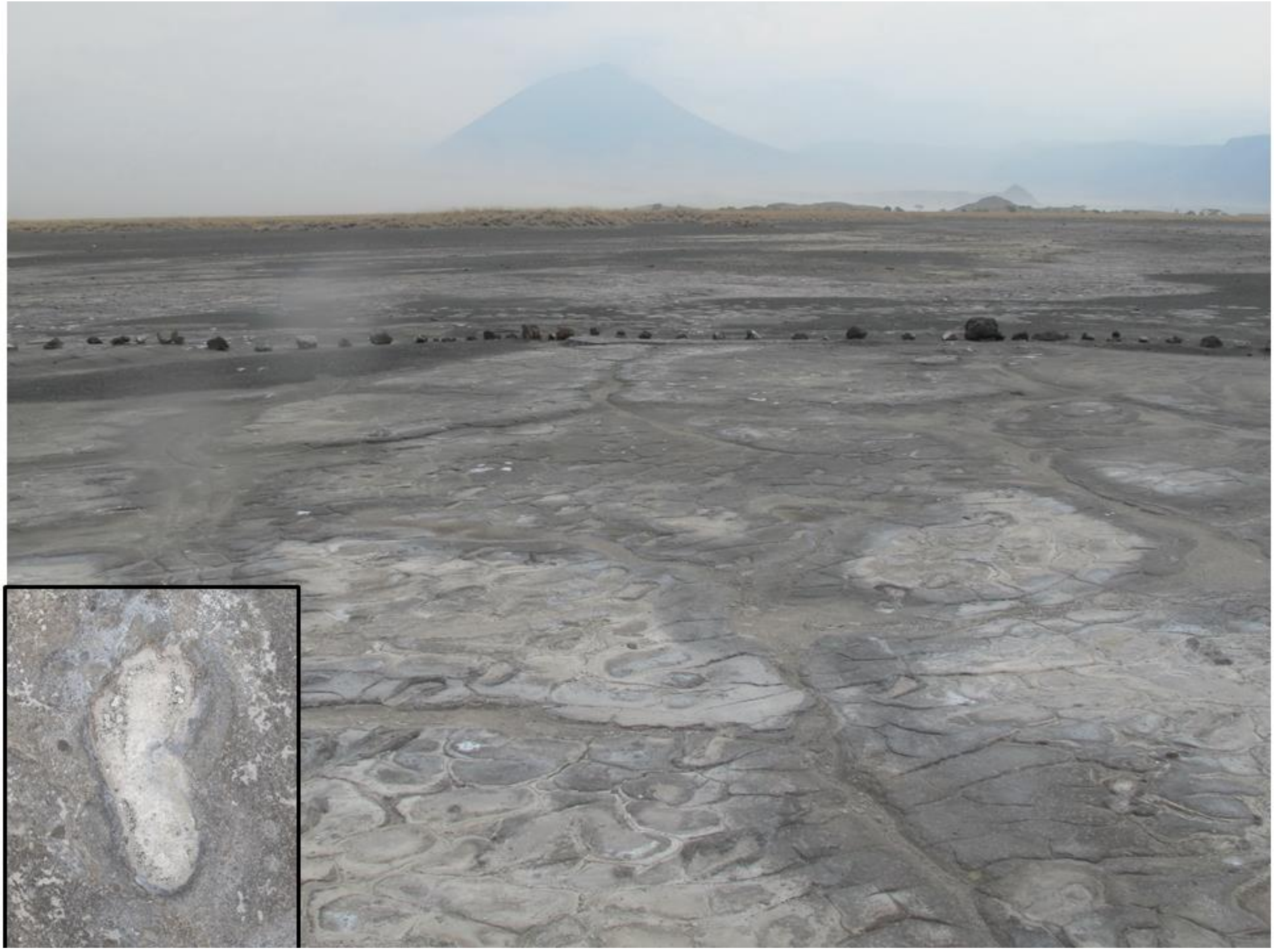

Figure 3 - The human footprints at Engaro Sera were naturally exposed and then fully cleared and left open in a remote area of northern Tanzania near Lake Natron; the active volcano of Oldoinyo Lengai is visible in background.

In situ preservation: reburial

Reburial is a proven preservation strategy and a reversible one, but it is a reluctant preservation option for most stakeholders. For, however beneficial reburial may be from a conservation perspective, it is generally viewed with skepticism or disfavor by those with legal authority over a site, and by those stake-holders, especially scientists and researchers, who want access to a site for study and education, or those who desire to exploit the site's economic value. Although the authors are strong advocates of reburial as a preservation strategy, they know well the difficulties attendant on its use. Aside from stakeholder reluctance, reburials are too often neglected or forgotten – an unfortunate consequence of being out of sight, and therefore out of mind. Thus the conditions for long-term preservation, especially the management context of the site, need to be carefully thought through. For discussion of a decision-making process and other aspects of reburial see Demas (2004) and other articles in that special issue of the journal devoted to reburial of archaeological sites.

If reburial or removal to a museum is chosen, compensating stakeholders for 'hiding' or removing the resource is critically important; this will certainly involve documentation and publication of the resource. The importance of excellent documentation (e.g. mapping, digital recording, photography) and publication cannot be overemphasized, since it may be the only form of preservation to survive, no matter what solution is chosen. Bennett et al. (2013) work though a decision-making process similar to that applied to the Laetoli trackway for the younger (1.5 My) footprint sites discovered at the site of Ileret in Kenya. Concluding that 'record and rescue' was the only viable choice, they make an especially strong argument for using the various methods of 3-D digital capture as a preservation strategy for track sites, especially those formed in soft sediments. But additional forms of compensation should be considered, such as creating replicas or exhibitions, which may be especially important to community stakeholders, and also taking molds of the tracks, if this can be done without damaging them, which can be used for scientific study as well as exhibition. A caveat is warranted about replication by taking a mold: while this can provide the most accurate representation of a track, it may cause damage to the impression and stain the surface, so needs to be undertaken by preparators with experience and tested on the substrate before-hand. As example, while the molds produced during the 1978-9 Leakey expedition at the Laetoli trackway resulted in superb casts of the footprints, problems resulted from the use of Bedacryl to consolidate the prints prior to molding (see Getty Conservation Institute, 1996: pp. 31-33).

A BRIEF REVIEW OF TRACKWAY CASE STUDIES

Examples of the many approaches that have been taken for preservation of fossil tracks and trackways, both human/hominin and dinosaur, are reviewed for a number of significant sites. It should be noted that while there are many publications about hominin and faunal track sites (see Kim et al., 2004; Lucas et al., 2007; and references therein), very few of these publication have anything to say about the state of preservation, conservation interventions that have been undertaken, and follow-up regarding current status. The sites reviewed here include the Laetoli hominid trackway in Tanzania, the human footprints found at the Willandra Lakes Region site, and the Dinosaur Stampede National Monument at Lark Quarry, both in Australia, all of which the authors have had professional involvement with, as well as other sites that demonstrate the complexity of issues and the uncertainties of being able to assure preservation over the long term. They provide useful lessons for anyone contemplating the options for preserving a fossil track site. While some of the scientific literature is cited, the intention of this paper is not to discuss the scientific, paleontological issues of the sites; rather, the intention is to elucidate the problems, options and decision-making considerations related to their long-term preservation.

Willandra Lakes Trackways, Australia

The human tracks in the Willandra Lakes Region, a UNESCO World Heritage Site in far western New South Wales, dated to some 20,000 years BP, are of great cultural significance to Aboriginal communities in the region and are of scientific importance with respect to the antiquity of human presence in Australia and as the largest collection of Pleistocene footprints in the world (Webb et al., 2006). Discovered in 2003, the site has revealed over 700 footprints and 23 trackways of men, women, and children on the shore of an ancient lake (Figure 4). The decision about how to protect the site and whether to open it to visitors involved long discussion between professionals and community members. Fortunately, decisions were not made hastily and wise council prevailed. Thus, the site is buried and protected against wind ablation and freeze-thaw cycles that undoubtedly would have destroyed the fragile surface within a short time (Figure 5), leaving open the option in the future to display the footprints to the public if an adequate solution for their preservation can be found. Instead the footprints are interpreted elsewhere within the World Heritage area and three tribal groups, the traditional owners, are responsible for the site, assisted by the New South Wales National Park Service (Johnson and Mintern, 2013). As with so many track sites, documentation has been central to trying to find patterns and interpret the complex trails.

Lark Quarry Dinosaur Trackway, Australia

In 1976-77, the Lark Quarry dinosaur trackway site, as of 2004 officially the Dinosaur Stampede National Monument, Lark Quarry, was discovered in central Queensland. This too is a site of exceptional importance as it records the only known stampede of dinosaurs (Thulborn and Wade, 1984). It was one of the first three places to be nominated to Australia's National Heritage List in July 2004. Some 4000 tracks in an area of 210 square meters feature unique evidence of small to medium size running bipedal dinosaurs, perhaps 150 in number, apparently stampeded by a large theropod, though interpretations differ, whose presence is known from eleven tracks. The site, dated to the Early Cretaceous Epoch some 95 million years ago, records individual animals as they ran swerving and crossing each other's path during a few seconds of time (Thulborn and Wade, 1984).

Figure 4 - The ancient lakebed and stark landscape setting in which the human footprints were discovered in the Willandra Lakes Region, as seen in 2007 with elders of the community assembled nearby.

Figure 5 -The decision was made by the traditional owners to rebury the Willandra Lakes footprints for their protection, seen here with a covering of sand and a sandbagged border.

Many of the tracks are extraordinarily well preserved in the fine-grained mudstone that was buried by a coarser grained sediment shortly after the event. A small representative part of the trackway was lifted and moved to the Queensland Museum, and this is likely the best preserved section that exists today.

Various misfortunes befell the excavated site after the decision was made to keep it exposed for public visitation despite the remoteness from population centers and poor access on unpaved roads. These have been described in detail (Agnew et al., 1989). The decision was apparently based on the drama of predator with prey in desperate flight so perfectly preserved in the record of the rock across a great span of time, but no realistic evaluation of tourism potential or sustainability was undertaken. While plans were developed and funds being secured for sheltering, the site was left exposed, though covered with bales of straw which caught fire during unsupervised construction of the protective roof structure, resulting in extensive loss of the thin secondary deposit of limonite that defined the trackway surface and one track was lost when a support column for the roof was placed on it (personal communication from excavator of site, Mary Wade). Perhaps as few as ten visitors in a week came in the first years, though kangaroos seeking shade under the open shelter (Figure 6) came in far greater numbers and some died on the surface. A number of tracks were souvenired as the site had no guardian. Additional problems were flooding of the surface, the accumulation of dust in the prints rendering them difficult to see, and a general inability of the site to be understood by the visitor. In 2001 a new, environmentally "green" building was constructed to totally enclose the trackway site (Figure 7). Well-designed raking lighting allows the tracks to be viewed more clearly than in natural daylight, which was the situation under the first roof (Figure 8). The importance of good lighting is too often neglected; tracks, being by nature shallow depressions, are often very difficult to see without raking light, which can lead to frustration, and even vandalism, on the part of visitors. Despite the positive aspects of the new shelter, it too was not without problems. Soon after opening to the public in 2002 one of two large rammed earth walls, intended to provide thermal stability for the interior climate, collapsed onto the visitor walkway and the tracks, fortunately at night when no visitors were present; presumably failure of the material resulted in the collapse. Again in 2011 instability in a wall caused the track site to be closed to the public.

Figure 6 - The first shelter constructed over the dinosaur tracks at Lark Quarry in 1979 was open on the sides allowing dust, kangaroos, and acquisitive visitors to enter.

Figure 7 - A new shelter, utilizing green technologies, was constructed over the Lark Quarry trackway site in 2002, with further retrofitting undertaken in 2014.

Figure 8 - Interior of the new enclosed shelter at Lark Quarry, with raking lighting along the walkway that allows better viewing of the tracks; detail shows close-up of tracks.

The lessons to be learned in the Lark Quarry case study are many, but principally they can be summarized as follows: Outdoor sites are exposed to the full impacts of natural deteriorative forces: meteorological, physical, chemical and biological. A site of this significance should be assessed for visitation potential before deciding to keep it open; it must be thoroughly documented and adequately protected after excavation and while funds are being secured for permanent sheltering, staffing, access and interpretation; a risk analysis should be undertaken with many kinds of inputs from specialists in their own fields, as for example, environmental ones (animal habitation of the shelter, flood, petrological fragility of the rock); unsupervised construction should never be allowed; systematic monitoring of condition must be undertaken over the long term; and stable funding is needed for maintenance of the site and its infrastructure. While the shelter and the current management structure appear to be protecting and interpreting the site and the surrounding environment, and new roads and marketing are encouraging greater visitation, only time will tell whether the limited number of visitors will be sufficient to justify and sustain the interventions.

Formby Point, England

These intertidal sites on the west coast of England, dating to about 5,500 years BP, are of high scientific value as they show the tracks of humans and animals such as deer, aurochs, and birds. Some 145 different trails at Formby alone have been noted. Accelerated beach erosion both exposes and destroys the tracks. Clearly in this instance the protection of sites is futile in the face of erosion by the sea. The sites are primarily research ones and photography of the footprints, recording their positions, and lifting and making casts of selected specimens has been an ongoing research activity and appropriate in the circumstances (Roberts et al., 1996).

Liujiaxia Dinosaur National Geopark, China

This site near the city of Lanzhou in Gansu Province was discovered in 1998. Paleontologically these Early Cretaceous tracks are noteworthy and the uplifted block on which the tracks are imprinted and the surrounding geology are dramatic, but visually and in terms of well-defined tracks the site is disappointing for the non-specialist visitor. As noted previously, however, the cachet of dinosaurs is such that a large protective structure was built over it in 2005 and nearby an interpretive center was under construction. Enquiry revealed that few visitors come and there was an air of neglect of the structure with evidence of roof leakage and deterioration (Figure 9). This example makes the point previously discussed, which is that without assessment of all factors that will affect the future of an exposed site, deterioration of the site and any infrastructure will inevitably occur. All too often the impulsive response, as with Lark Quarry, to an important find is to open it for visitors whereas a period of assessment and reflection may well bring forth more sustainable alternatives. As is also typical, continued excavation by the scientists have revealed more tracks, leading to more conservation dilemmas. These are being reburied and maintained by the authorities, but require frequent renewal of burial fill that is eroded out with each rain on the steep incline of the uplifted rock (Figure 10). The new interpretive museum at the bottom of the hill may bring better management of the site, but as of January 2016 it was still not completed.

Laetoli Hominid Trackway, Tanzania

The Laetoli trackway site, on the edge of the Serengeti in Tanzania and near the famous hominid site of Olduvai Gorge, is one in which the authors were involved over a six-year period, from 1993-1998. The site, discovered by Mary Leakey and team in 1977, was excavated, documented, molds and casts made, and reburied again for preservation against erosion and damage from large animals (Leakey and Harris, 1987). The reburial mound however, proved to be a fertile nursery for acacia tree growth and because the site was not monitored or maintained, within little more than five years trees had grown vigorously and root penetration, it was feared, would destroy the fragile prints if allowed to grow unchecked. A trial excavation in 1992 by the Department of Antiquities showed extensive root growth over and into the trackway (Figure 11).

Figure 9 - Interior of the Liujiaxia Dinosaur Trackway site shelter, which encloses the uplifted block with tracks, at lower left, and interpretive displays.

Figure 10 - Excavated dinosaur tracks outside the sheltered tracks at Liujiaxia, protected with a reburial and sandbags.

Figure 11 - A trench excavated in the reburied Laetoli trackway in 1992 by the Department of Antiquities to preliminarily assess the extent of root intrusion of acacia trees; one stump visible in left foreground with its roots penetrating the trackway.

The trackway has been securely dated at 3.6 Mya by potassium-argon dating of biotite crystals in the tuff from volcanic ash fall (Hay, 1987). The trackways, which consist of 3 trails of hominids (Figure 12), likely *Australopithecus afarensis*, have high scientific significance: "The hominid footprints at Laetoli comprise one of the most unique and important discoveries in the history of human paleontology. It is most unlikely that any similar resource will be discovered and recovered in the foreseeable future, if ever again. This singular discovery plays a crucial role in our understanding of the evolution of our own species" (Lovejoy and Kelley, 1995: p.28). Its scientific value lies in the direct evidence of bipedalism and gait at 3.6 Mya; the cultural value is as a symbol of the rise of humanity to dominance on earth today and the fact that people respond powerfully to human traces such as the image of the first footprint on the Moon.

A systematic assessment of the options for conservation of the site was undertaken, premised on re-excavation and removal of the trees and careful extraction of roots as the initial step. The various options considered at the time and the decision-making process have been reported elsewhere (Demas and Agnew, 2006). Briefly, these were the three options, noted previously: reburial and maintenance to prevent revegetation by deep-rooted acacia trees; sheltering and presentation to the public; and lifting the tracks and removal to the regional museum in Arusha or to the National Museum in Dar es Salaam.

The management context, specifically including the personnel and expertise to monitor and maintain the site, was paramount in decision-making. Sheltering was not considered viable for many reasons: lack of resources, trained personnel, roads, and difficulty of access; and the fragility of the tuff and the impact of continuous cleaning of the prints on that fragile surface. Removal to a museum was the option favored by many paleoanthropologists who often equate it with the universal practice of excavating rare fossil bones and displaying or storing them in a museum. There were many

Figure 12 - Southern portion of the Laetoli trackway, comprising trails of three hominids, two individuals walking in tandem in the right-hand trail, and hipparion tracks crossing hominid prints in lower right.

problems with this option: lack of proper and safe storage area in both the national and particularly the regional museum in Arusha, and the grave risks to the tracks posed by removal of the fragile prints in pieces (without complete consolidation of the tuff) and transportation from a remote location; moreover, to consider the Laetoli hominid tracks apart from the landscape in which they were created and the other animals that inhabited that landscape and left their tracks in far greater abundance than the hominids is to undermine their real significance. Scientific investigations of the tracks themselves and the trails they made are best done on the excellent set of casts made in 1978-79 when they were initially excavated.

Reburial, in conjunction with photogrammetry and photography of the individual prints and trackway, was therefore chosen as the most appropriate option at the time given the remoteness of the site and the lack of infrastructure and personnel to monitor and maintain a shelter. Furthermore, it is a reversible intervention should the circumstances change that make other options viable in the future. Thus, with concurrence and participation of the Antiquities Department of Tanzania, after excavation, conservation and detailed recording (see Getty Conservation Institute, 1996), the site was reburied (Figure 13).

Realizing the need for public exhibition and community outreach our project undertook a permanent display at the Olduvai Museum. This was centered on a replica of the cast of the trackway that Mary Leakey had made during the original excavation in 1979 (Figure 14). The exhibition, with information in English and Swahili, focused on the discovery of the trackway, its significance and conservation, and an explanation of the reasons for its reburial. Along with extensive re-casting of original casts and documentation of the trackway, the exhibit was considered an important strategy to compensate the scientific and local communities for not keeping the trackway open for study and visitation.

A political decision in recent years has led to new plans for re-excavation of the trackway and construction of a shelter and interpretive center at the site (Anonymous, 2014). With new management, now under the Ngorongoro Conservation Area Authority in which the track site is located, and a realistic risk assessment of sheltering and the visitation potential, this may be a solution, but a transparent demonstration of this is warranted. On-going field and research activity in the area can also be an important way to help protect a site, but is not always sustainable in the long term – researchers move on and research interests change. Protection is the necessary and avowed purpose of a shelter, but few shelters are ever built without visitors as a principal objective. Maintaining all these factors – good management, appropriate conservation and protection, visitation, and research in the right balance and for the long-term in a remote site is often simply not possible.

Courtedoux dinosaur track site, Switzerland

The Jurassic dinosaur tracks found in Canton Jura, Switzerland, during the course of investigations for a highway (A16) present an interesting example of working through an assessment process to determine the future of the site (Marty et al., 2004, 2007). The importance of the sites both nationally and internationally is well demonstrated and the potential values of the site (scientific, research, education and economic) are explored. The initial plans were to keep the sites open for public viewing, continue research and excavation, provide a protective roof and interpretive center, all of which will entail large expenditures to divert the highway over the track sites (a 'highway bridge'). The tracks cover a very extensive area and those track sites that were not destroyed in the construction of the highway were reburied, pending a final decision about their future (Marty et al., 2011). In their interesting review of dinosaur sites in Portugal, Santos et al. (2008) note that the Carenque (Pego Longo) dinosaur track site, also in the line of a highway, was covered pending long-delayed implementation of a decision to save the site by tunneling below it. Although the authors suggest that the covering was unfortunate since the site remained inaccessible to researchers, it would seem a wise decision in both these cases, for their protection.

For the Highway A16 sites, it is not clear what explicitly was being proposed for protection and conservation other than "protection by a roof or other adequate structure." The 2004 paper cites the publication on Lark Quarry dinosaur stampede by Agnew et al. (1989) as an example of a track site that

Figure 13 - After conservation, the Laetoli trackway was reburied under multiple layers of sand and geosynthetic materials, here showing several layers on the southern portion of trackway.

Figure 14 - Cast of the Laetoli trackway, from the original cast made by Mary Leakey's team in 1978, along with didactic material about the trackway and its conservation was created for the Olduvai Museum in 1997.

"has been protected from normal processes of erosion by a roof" (Marty et al., 2004: p.45). However, as described in the article, the roof actually resulted in more damage rather than protection (for subsequent developments at the site see Lark Quarry discussion above). The mere fact of a roof over a site is no guarantee of protection and natural processes of erosion are by no means the only threats to a track site.

CONCLUSIONS

It is clear that neither an in situ or ex situ approach to fossil preservation is without problems nor will one or the other be effective in all cases. In that sense the notion of 'options' is merely an artifice to draw lessons from case studies, thereby allowing the issues to be elucidated. Fossil bones and for that matter other three dimensional fossils do not in general present the long-term preservation dilemmas that track sites do – they almost always are excavated if important enough and taken to the laboratory for further preparation, conservation, storage or display. There are, however, exceptions to this, and two were noted earlier: Wadi el Hitan and Dinosaur National Monument. Rare or spectacular finds, such as a complete *Tyrannosaurus rex* skeleton, are certainly removed, as are early hominin remains because of their high scientific and social value. Track sites on the other hand present particular problems: the scale may be large, and storage facilities for removed track sites are usually inadequate, as previously mentioned; moreover, the cost of lifting and transporting an entire trackway, as was proposed for Laetoli, can be technically challenging if only from a geotechnical and engineering point-of-view, prohibitively expensive, and removes the site from its larger landscape context.

In situ conservation with high level documentation (molding and casting, photogrammetry, photography as appropriate) tends therefore to be the preferred option. The question of how best to do this then becomes of paramount importance. When the significance of the site is high or the tracks are those of the popular and charismatic dinosaurs, the temptation to display them to the public may blind decision makers to the need for sustainable measures of preservation and interpretation. Track sites in general require robust and creative interpretation to make them understandable and interesting to the average visitor. Seldom are all the potential threats, or the constraints of funding over the long term, staffing and other management considerations taken fully into account. In other words, what we see frequently is a pattern of excavation, research and study, followed by touristic development, with very limited assessment of conservation approaches and considerations of long-term preservation. The options of reburial, sheltering, ex situ preservation, and the need for expertise, testing of materials or additional studies, such as on weathering rates, should be considered from the outset since funding for preservation can be slow or difficult to secure with delays and consequent damage to the site. While paleontologists recognize that exposure to weathering and erosion are destructive and that these sites are fragile, it is in fact quite rare to find technical conservation studies undertaken for track sites. As example, the practice of painting tracks so they are more visible to public is symptomatic of the visual challenges presented by track site, but the intervention taken to address it may be harmful or obscure details of the tracks, and is not discussed. This is of particular interest and importance as fossil and track sites are increasingly placed under the umbrella of the emerging concepts of geoscience, geoconservation, geotopes, geo-parks, and geoheritage (e.g., Marty et al., 2004; Santos et al., 2008; Bennet et al., 2013). Track sites, however, would benefit equally, if not more, from methods employed and lessons learned in the field of archaeological site conservation and management.

Fossils and fossil sites of all kinds will continue to be found. Those of lesser interest to paleontologists will be excavated and either buried again after having been recorded or sometimes abandoned to erode away. Scientifically and culturally valuable sites will receive special attention. It is these cases that require a careful and complex decision–making analysis based on thorough understanding of their significance for different constituent stakeholders, investigation of environmental conditions and threats, and long-term human and financial resources. If this process is not followed the weakest link in the chain of considerations will eventually come to the fore and lead to an inexorable decline of the site and degradation of its condition and loss of values as the integrity diminishes. And since even the most rigorous assessment, planning and conservation approaches can be upended through unanticipated political interventions or changes in managing authority and personnel, multifaceted recording and documentation of sites is a sine qua non of their preservation.

REFERENCES CITED

Agnew, N., H. Griffin, M. Wade, T. Tebble, and W. Oxnam. 1989. Strategies and techniques for the preservation of fossil tracksites: an Australian example; pp. 397–407 in D. D. Gillette and M. G. Lockley (eds.), Dinosaur tracks and traces. Cambridge University Press.

Anonymous. 2014. Tanzania: Grand Laetoli Footprints' Museum to Be Built in 2015. Arusha Times.

Bennett, M. R., P. Falkingham, S. A. Morse, K. Bates, and R. H. Crompton. 2013. Preserving the impossible: Conservation of soft-sediment hominin footprint sites and strategies for three-dimensional digital data capture. PLOS ONE 8:e60755.

Boaz, N. T., and R. L. Ciochon. 2004. Dragon Bone Hill: An Ice-Age Saga of *Homo erectus*. Oxford University Press, New York, USA, 253 pp.

Bradley, S. M., and A. P. Middleton. 1988. A study of the deterioration of Egyptian limestone sculpture. Journal of the American Institute for Conservation 27:64–86.

China Heritage Project. 2005. The renewed search for Peking Man. China Heritage Quarterly. Available at http://www.chinaheritagequarterly.org/articles.php?searchterm=003_pekingman.inc&issue=003. Accessed November 10, 2016.

Demas, M. 2004. "Site unseen": the case for reburial of archaeological sites. Conservation and Management of Archaeological Sites 6:137–154.

Demas, M. 2013. Protective shelters for archaeological sites; pp. 57–133 in T. Roby and M. Demas (eds.), Mosaics in Situ: An Overview of Literature on Conservation of Mosaics in Situ. Getty Conservation Institute, Los Angeles, USA.

Demas, M., and N. Agnew. 2006. Decision making for conservation of archaeological sites: The example of the Laetoli Hominid trackway; pp. 64–72 in N. Agnew and J. Bridgland (eds.), Of the Past, for the Future: Integrating Archaeology and Conservation, Proceedings of the Conservation Theme at the 5th World Archaeological Congress, Washington, D.C. Getty Publications.

Getty Conservation Institute. 1996. Laetoli Project: Conservation of the Hominid Trackway Site at Laetoli, Tanzania: Report on the 1995 Field Season (July 3- September 2, 1995). Getty Conservation Institute, Los Angeles, USA, 260 pp.

Hay, R. L. 1987. Geology, dating, and palynology: geology of the Laetoli area; pp. 23–47 in M. D. Leakey and J. M. Harris (eds.), Laetoli: A Pliocene Site in Northern Tanzania. Oxford Science Publishers, Oxford, UK.

Howie, F. M. P. 1979. Museum climatology and the conservation of palaeontological material. Special Papers in Palaeontology 22:103–127.

Johnson, H., and R. Mintern. 2013. Managing Australia's world heritage in the Willandra Lakes Region; pp. 102–107 in P. Figgis, A. Leverington, R. Mackay, A. Maclean, and P. Valentine (eds.), Keeping the Outstanding Exceptional: The Future of World Heritage in Australia. Australian Committee for IUCN Inc., Sydney, Australia.

Kim, J. Y., K.-S. Kim, S. I. Park, and M.-K. Shin. 2004. Proceedings of the International Symposium on the Quaternary Footprints of Hominids and Other Vertebrates. 175 pp.

Leakey, M. D., and M. J. Harris. 1987. Laetoli, a Pliocene Site in Northern Tanzania. Oxford University Press, Oxford, UK, 561 pp.

Lovejoy, C. O., and C. A. Kelley. 1995. The Laetoli Footprints: A Review of Their Scientific Status in 1995 (Report Prepared for the Getty Conservation Institute). Getty Conservation Institute, Los Angeles, USA, pp.

Lucas, S. G., J. A. Spielmann, and M. G. Lockley. 2007. Cenozoic Vertebrate Tracks and Traces: Bulletin 42. New Mexico Museum of Natural History and Science, Albuquerque, USA, 339 pp.

Marty, D., G. Paratte, C. Lovis, M. Cattin, and W. A. Hug. 2011. Status quo of dinosaur track excavations on highway A16 (Canton Jura, NW Switzerland) with emphasis on documentation, research, and geoconservation; pp. 38 in A. Richter and M. Reich (eds.), Dinosaur Tracks 2011, An International Symposium, Obernkirchen, Abstract Volume and Field Guide to Excursions. Universitäts-drucke Göttingen, Göttingen, Germany.

Marty, D., L. Cavin, W. A. Hug, P. Jordan, M. G. Lockley, and C. A. Meyer. 2004. The protection, conservation and sustainable use of the Courtedoux dinosaur tracksite, Canton Jura, Switzerland. Revue de Paléobiologie 9:39–49.

Marty, D., J. Ayer, D. Becker, J.-P. Berger, J.-P. Billon-Bruyat, L. Braillard, W. A. Hug, and C. A. Meyer. 2007. Late Jurassic dinosaur tracksites of the Transjurane highway (Canton Jura, NW Switzerland). Bulletin Für Angewandte Geologie/Schweizerische Vereinigung von Petroleum-Geologen Und Ingenieuren 12:75–89.

Roberts, D. L. 2008. Last interglacial hominid and associated vertebrate fossil trackways in coastal eolianites, South Africa. Ichnos 15:190–207.

Roberts, G., S. Gonzalez, and D. Huddart. 1996. Intertidal Holocene footprints and their archaeological significance. Antiquity 70:647–651.

Rodriguez-Navarro, C., E. Sebastian, E. Doehne, and W. S. Ginell. 1998. The role of sepiolite-palygorskite in the decay of ancient Egyptian limestone sculptures. Clays and Clay Minerals 46:414–422.

Santos, V. F., C. M. da Silva, and L. A. Rodrigues. 2008. Dinosaur track sites from Portugal: Scientific and cultural significance. Oryctos 8:77–88.

Shelton, S. Y., R. C. Barnett, and M. D. Magruder. 1993. Conservation of a dinosaur trackway exhibit. Collection Forum 9:17–26.

Stanley-Price, N., and F. Matero. 2001. Special Issue on Protective Shelters. Conservation and Management of Archaeological Sites, 5(1-2). James & James, London, UK, 115 pp.

Webb, S., M. L. Cupper, and R. Robins. 2006. Pleistocene human footprints from the Willandra Lakes, southeastern Australia. Journal of Human Evolution 50:405–413.

Xing, L., D. Li, P. L. Falkingham, M. G. Lockley, M. J. Benton, H. Klein, J. Zhang, H. Ran, W. S. Persons, and H. Dai. 2016. Digit-only sauropod pes trackways from China – evidence of swimming or a preservational phenomenon? Scientific Reports 6.

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SCANNING ELECTRON MICROSCOPE (SEM) SHOWS UNDESIRABLE EFFECTS OF ULTRASONIC CLEANING ON RECENT MOLLUSK SHELLS

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ABSTRACT

We evaluated the effects of ultrasonic cleaning on mollusk shells using scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis. The objective was to investigate the effects of this cleaning approach on the organic layer of the shells (the periostracum) and to assess the efficacy of a thin coating of consolidant to protect shells from vibrations. We found that ultrasonic cleaning caused abrasion of the shell surface. Treated specimens showed a flaky exterior, while non-treated specimens showed a more homogenous surface. Pre-treatment with TEOS-based consolidant did not prevent loss of the superficial layer and precipitated solid crystals on the surface. Our findings indicate that ultrasonic cleaning should be used with caution for fragile specimens because it can substantially alter the surface of mollusk shells.

Keywords: mollusk; shell; ultrasonic cleaning; conservation; scanning electron microscope

RESUMO [in Portuguese]

Avaliamos os efeitos da limpeza com ultra-sons em conchas de moluscos usando microscopia eletrónica de varrimento (MEV) com análise de raios-X de energia dispersiva (EDX). O objetivo foi investigar os efeitos dessa abordagem de limpeza sobre a camada orgânica das conchas (o periostracum) e avaliar a eficácia de um revestimento fino de consolidante para proteger as conchas das vibrações. Verificou-se que a limpeza ultra-sónica causou abrasão da superfície da concha. Os espécimes tratados mostraram um exterior mais quebradiço, enquanto os espécimes não tratados apresentaram uma superfície mais homogênea. O pré-tratamento com consolidante TEOS não impediu a perda da camada superficial e precipitou cristais sólidos na superfície. Os nossos resultados indicam que a limpeza ultra-sónica deve ser usada com cuidado para espécimes frágeis, pois pode alterar substancialmente a superfície de conchas de moluscos.

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INTRODUCTION

The anatomical and functional characteristics of mollusk shells have long played an important role in taxonomic studies to identify species (Harper, 1997). However, interest has recently broadened intensively to encompass issues such as developmental mechanisms (Araujo et al., 2014), ultrastructure (see a review in de Paula and Silveira, 2009), and molecular analysis (Geist et al., 2008).

Shells are an efficient tool for surveying biodiversity due to their easy handling and their marked morphological characteristics. Mollusk shells have two layers of natural composition: the periostracum and the ostracum. The periostracum, the outermost layer of shells, consists entirely of organic material, chiefly proteins. As this delicate coating (conchiolin) covering specimens is useful for zoological and taxonomic identification, its conservation is of particular relevance. See Harper (1997) for in depth data regarding the differentiation process and also for specific studies based on the use of SEM technologies to identify species (Korniushin, 2000). Recently developed techniques make the periostracum of mollusks a key character for diagnosing species, in particular in museum specimens (Leonel et al., 2006). The ostracum is the layer below the non-calcified periostracum and it consists of several calcified layers with a wide variation in their microstructures The ostracum often consists of prismatic aragonite crystals, but it is calcitic in most pteriomorph bivalves and in some gastropod taxa (Furuhashi et al., 2009).

Mollusk shells housed in museum collections may suffer various alterations. The most frequent of these is cracking, caused by rapid changes in temperature and humidity (Child and Buttler, 1996; Morton, 2006). Shells may also undergo chemical destructive processes such as efflorescence (also called Bynesian decay; Tennent and Baird, 1985; Sturm et al., 2006; Caracanhas Cavallari et al., 2014). As shells are widely used in biological research, the importance of their long-term conservation cannot be overlooked (Leonel et al., 2006; Sturm et al., 2006).

Removing dust, dirt and biological contaminants (such as mould, fungi, and bacteria) from shells with a cleaning treatment improves conservation (Sturm et al., 2006; De Prins, 2007). The cleaning process also highlights distinguishing features of shells, particularly on the aperture area, which is often covered with soil remnants. One of the most commonly used treatments to remove dirt and soil is mechanical friction. However, as this method is not suitable for micromollusks, cleaning could be performed using an ultrasound tank, as described by other authors (Smith, 1962; Sturm et al., 2006). Studies regarding cleaning of shells, however, are scarce.

The use of an ultrasonic tank is relatively common in the restoration of inorganic materials and preparation of fossil specimens in order to remove dirt and separate the matrix from the fossil (Kuban, 2004). One of the advantages of this technique is the simplified handling of the sample since the vibrational effect driven through a liquid solution induces cavitation, that is, the formation of micro-bubbles that grow and collapse rapidly (Suslick, 1989). These effects cause solid surface erosion or eventual breakage of particles, helping to remove the soil and dirt (Ensminger and Stulen, 2008:327; Santos et al., 2011).

The Natural History Museum of Barcelona (MCNB) recently launched a project to promote citizen participation in the study of Catalan terrestrial malacofauna. A representative collection of this fauna is being assembled as a new resource to provide visitors with reliable information to identify their own samples. As specimens in the reference collection must be as clean as possible, we conducted a thorough cleaning process of the whole collection.

The cleaning treatments followed general conservation criteria (AIC, 1994; ECCO, 2003; ICOM-CC, 2006) and were carried out by one of the authors (MR) during the course of a Master's Degree in Management of Conservation-Restoration Projects at the University of Barcelona in 2013. Throughout this process, the opportunity arose to collaborate with the Scientific and Technologic Centre at the University of Barcelona (CCITUB) and use of their scanning electron microscope (SEM). Because only one SEM session was carried out, we scanned only a small number of specimens. Extensive comparative studies were ruled out because the use of SEM was not planned when the project was developed. We therefore present this experiment as a preliminary work.

The goal of this study was to evaluate the suitability of cleaning micro-mollusk shells (<10 mm) through immersion in ultrasonic baths. Factors taken into account were cleaning effectiveness, the physical integrity of treated samples (the emergence of micro-fissures, abraded surfaces, flaking or desquamation), and the role of a pre-consolidation treatment to protect the physical integrity of the shells.

MATERIALS AND METHODS

For this study we chose three specimens in a good state of conservation (physical integrity) belonging to a common species of terrestrial mollusk *Chondrina tenuimarginata* (Gastropoda: Pulmonata: Chondrinidae - accession number MZB 89-1041 from the MCNB collection; Figure 1).

Each shell underwent different direct conservation processes (Table 1):

Sample 1 (S1): A non-treated sample (control sample) for comparing the effects of cleaning and to observe the natural, unaltered morphology of shells.

Sample 2 (S2): An exclusively ultrasonically cleaned sample.

Sample 3 (S3): A pre-consolidated and ultrasonically cleaned sample.

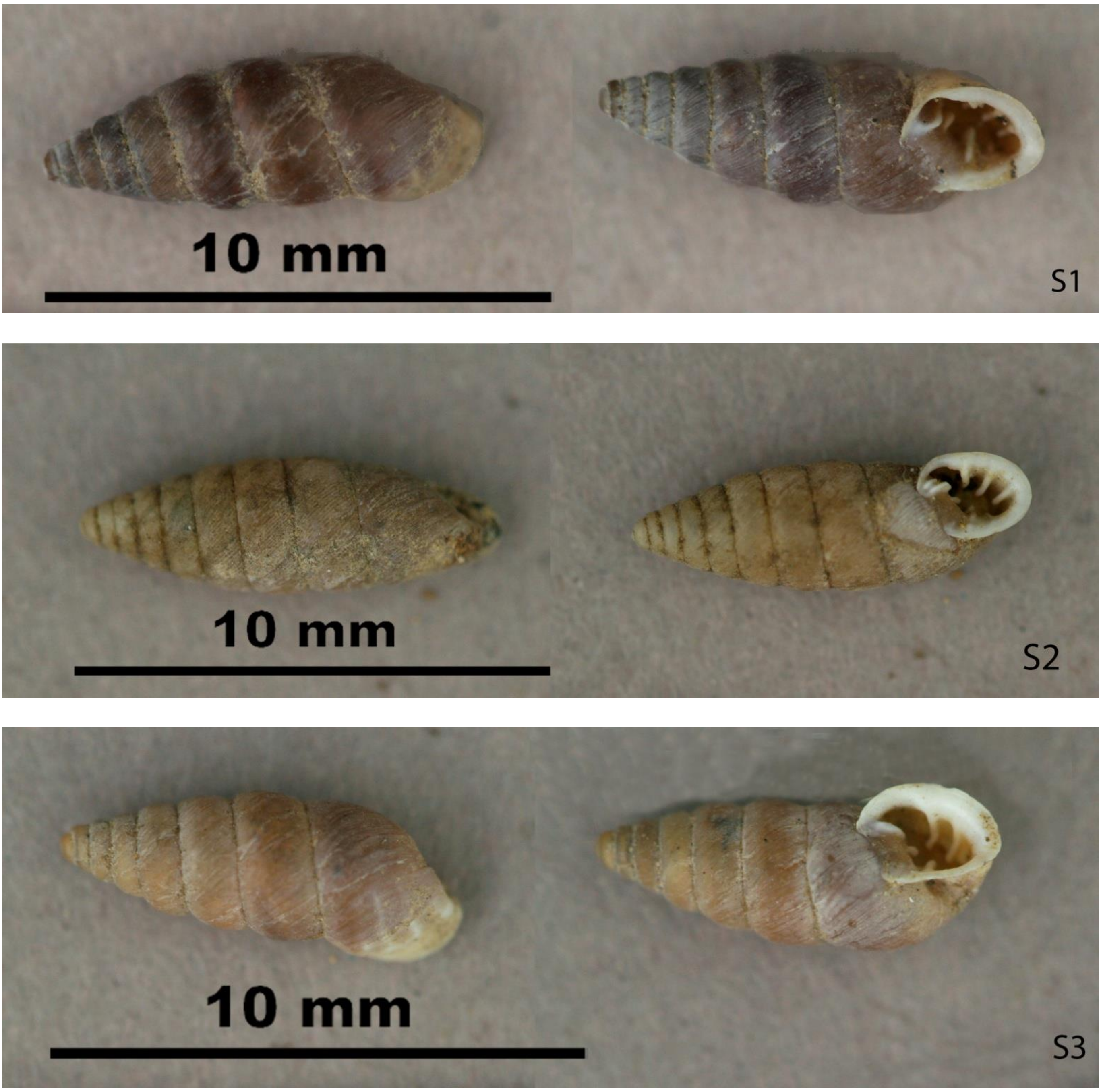

Figure 1 - Images of the three samples *Chondrina tenuimarginata* before treatment. Image by Marina Rull Aguilar.

Table 1 - Summary of treatments applied to samples.

Sample	Consolidation	Ultrasonic cleaning / Neutralization
S1 Control sample	**NO**	**NO**
S2	**NO**	**YES**
S3	**YES**	**YES**

Pre-consolidation treatment (S3) was done using a TEOS-based consolidant, ethyl silicate Estel 1000® (by CTS). The coating was applied using a paintbrush, the most commonly used procedure for consolidation treatments in natural history collections. Before applying the cleaning treatment, the consolidant was allowed to cure for a month (silicate polymerization). The siliceous consolidant was chosen since it allows good penetration due to its formulation and the small dimensions of the monomer seeping into cavities, cracks and pores without a plasticizing effect (Tennent and Baird, 1985; Öztürk, 1992; Morton, 2006; Sturm et al., 2006; De Prins, 2007), allowing superficial cleaning after consolidation. Several studies have shown the effectiveness of TEOS-based consolidants applied on stony supports of archaeological and architectural objects (Price, 1996; Rodriguez-Maribona and Cano, 2000; Meyer and Smith, 2008). TEOS-based consolidants have usually been used in the consolidation of siliceous materials but their effectiveness has also been tested filling narrow voids between calcite grains and, eventually, locking particles undergoing granular disintegration in limestone (Danehey et al., 1992; Price, 1996:55; Ruedrich et al., 2002). Thus, we considered that the use of a TEOS-based consolidant would penetrate the calcareous substratum of the shell.

We discarded the use of other consolidants suggested in previous studies (Sturm et al., 2006; De Prins, 2007). These are usually applied as a protective coating that consolidates by adhesion and creates an external layer similar to varnish with a low penetration capacity. This method does not allow subsequent surface cleaning (see Morton, 2006, for examples of protecting coatings for conservation and prevention of periostracal loss in museum collections). In any case, the use of consolidants and coatings in natural history specimens should be fully justified because it can interfere with future analysis (Sturm et al., 2006).

Cleaning consisted of sonicating samples for 60 seconds in a solution of distilled water with 2% neutral soap Derquim ®LM 02 to break the surface tension of water. Samples were neutralized in a solution of distilled water for 60 seconds. Ultrasound treatment was carried out in an ultrasonic tank Branson 8200 at a frequency of 40Hz and a voltage of 120v. Unfortunately, we were unable to control for other parameters (such as frequency, intensity or temperature) due to the technical limitations of the equipment.

To assess the qualitative dirt level before and after cleaning, we observed the shells using a stereomicroscope Kyowa Optical model SD-2PLQ.

All the experimental samples were directly examined without prior preparation (Cortadellas et al., 2012) using a SEM (model Quanta, 200 XTE 325/D8395 series, manufactured by FEI Company, Netherland) at the CCITUB facilities. The images were taken using the detector LFD at different magnifications (200 X to 1,537 X) as well as with "high vacuum mode" at 20KV of HV (high voltage) and working distance (WD) 9.6 mm, 9.7 mm, 9.8 mm and 10.2.

Up to five microanalysis for sample are performed with Energy Dispersive X-ray (EDX, included to the SEM microscope) and EDAX Genesis as the software for detecting chemical elements.

RESULTS

Observations using a stereomicroscope at 4X magnification allowed a qualitative evaluation of dirt level. After cleaning treatment, the shells presented a low dirt level and alterations were not visible. However, electron microscopy showed clear differences between samples.

Observation of sample 1 under SEM (control sample, Figure 2, S1) showed that the surface was quite homogeneous but irregularities were visible, such as desquamation consisting of subjacent layers in a grainy and crystallized texture. Spot chemical analysis (EDX) also detected superficial deposits, mainly non-metallic elements such as oxygen, carbon, and potassium, with predominance of calcium and very low representation of metallic elements such as aluminum and iron. Dirt and soil appeared chiefly in the sutures and mostly in the aperture. No fissures or cracks were observed.

Sample 2 (ultrasound cleaning treatment only, Figure 2, S2) showed a relatively homogeneous surface but generalized erosion of the outside shell. It presented detachment of the outermost layer, exposing a grainy and crystal texture, visible in the affected zones. Where the outermost layer was conserved, it appeared darker in the images. Small deposits of irregular morphology were seen on the surface. The chemical analysis identified these deposits as a mixture of non-metallic elements such as oxygen, carbon, potassium, sulphur, phosphorus, sodium, and manganese, but with a notable predominance of calcium. These elements may be the remains of external dirt that ultrasonic cleaning treatment failed to eliminate.

Several microanalysis carried out on the grainy surface gave the same result.

The elements identified were oxygen, carbon and chiefly calcium.

The aperture seemed clean, no significant presence of dirt is observed on the rest of the shell. No fissures or cracks were observed.

Sample 3 (consolidant and ultrasound treatment, Figure 2, S3) presented an heterogeneous surface with consolidant deposits discontinuously distributed in a quartered way, very superficially and especially on sutures and in the aperture. Chemical analysis confirmed the composition of the deposits as silica (Figure 3.1). We observed physical degradation on the surface with irregularities, such as desquamation, small orifices and erosion of the outermost layer especially in the exposed areas. Under higher magnification, we observed detachment of the superficial layer that exposed subjacent layers of crystal and a grainy texture (Figure 3). The elements detected in the grainy zones were basically non-metallic: oxygen, carbon, and a notable predominance of calcium (Figure 3.2). No fissures or cracks were observed, nor were superficial calcium deposits seen. Consolidant deposits may cover possible dirt remains, especially on the aperture and sutures. No penetration of consolidant into the shell was observed.

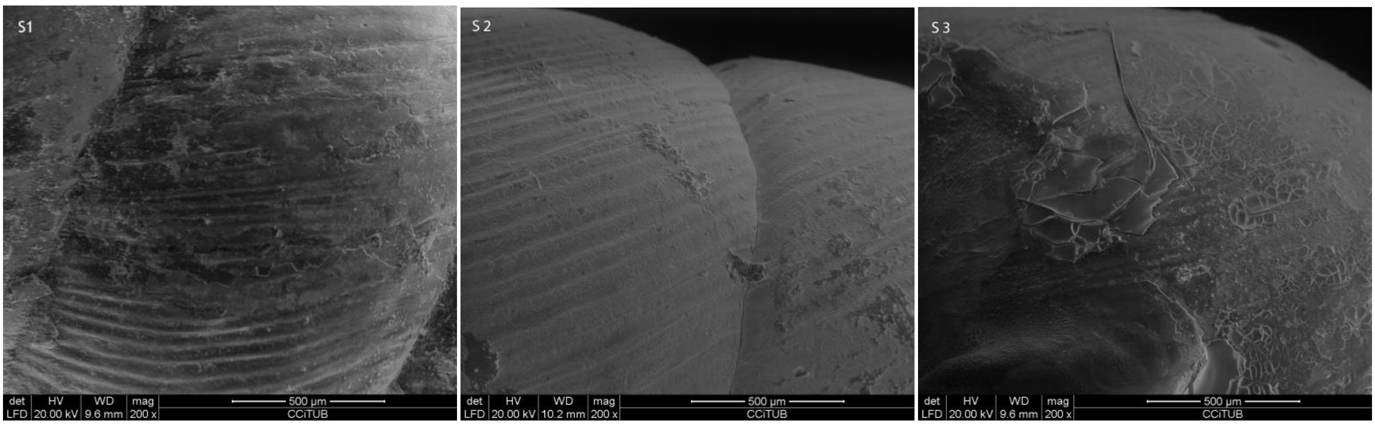

Figure 2 - SEM images of surface morphology of mollusk samples. S1) Untreated surface. S2) Abraded surface after ultrasonic cleaning treatment. S3) Residues of silica on surface after consolidation and ultrasonic cleaning treatments. Images by Cristina Ruiz-Recasens. Section of Conservation-Restoration. University of Barcelona.

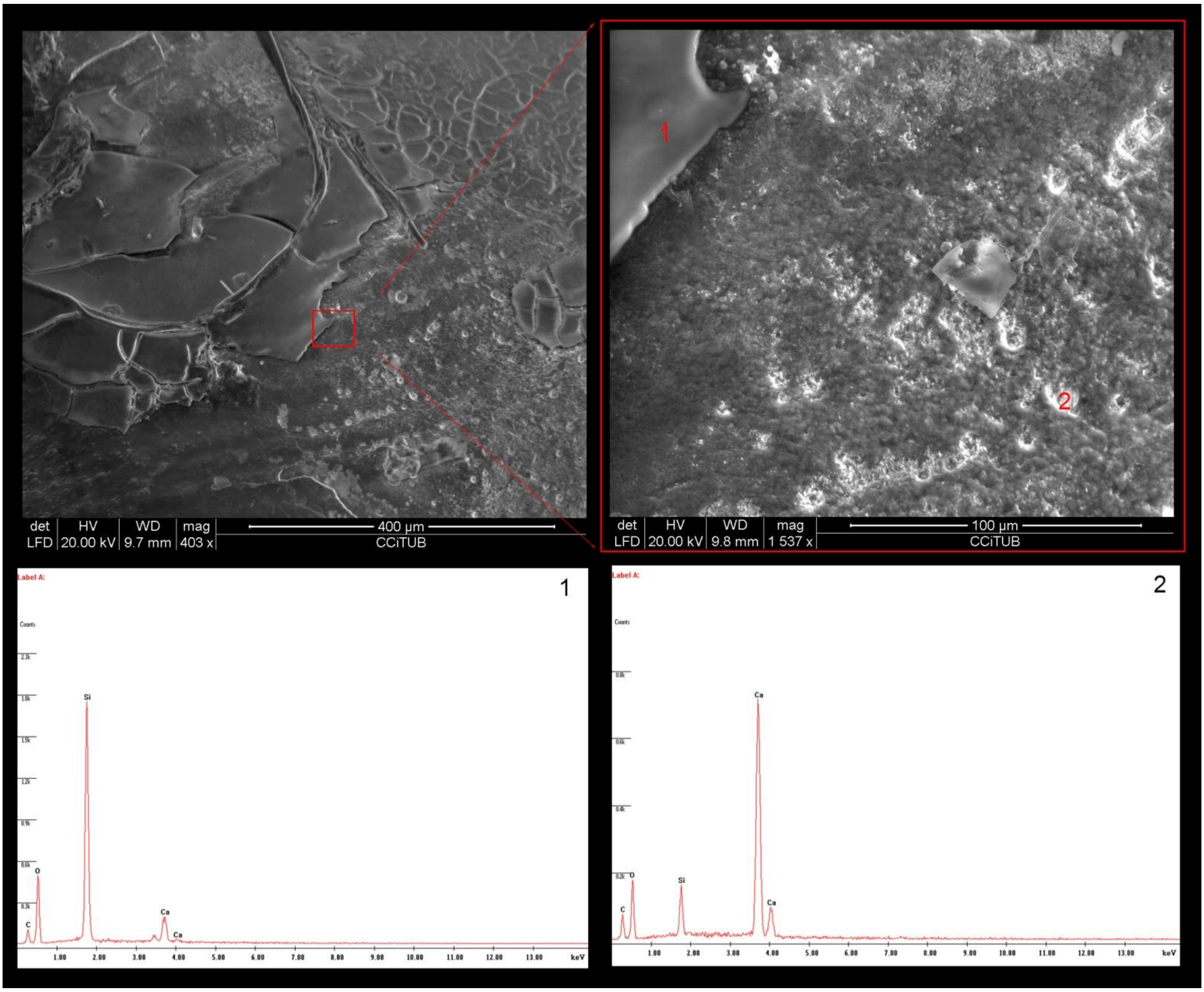

Figure 3 - SEM surface images of sample 3 after consolidation treatment. The numbers indicate the spot positions of the EDX microanalysis 1 and 2. The crystals are solid silica (1) and calcium (2), probably calcium carbonate substrate. Images by Cristina Ruiz-Recasens. Section of Conservation-Restoration. University of Barcelona.

DISCUSSION

Our findings suggest SEM is a good technique to evaluate the effects of ultrasonic cleaning (Stuart, 2007; Juanes Barber and Martín de Hijas Díez, 2008) and show that the ultrasonic cleaning procedure applied in this study had relatively good results with a decrease in dirt remains. However, the cleaning procedure had an undesirable effect on the surface of the shell: degradation was evident on treated samples, although no adverse effects were observed on a structural level (cracks or fissures). Interestingly, no degradation was visible under examination with a stereomicroscope.

The identification of calcium in the EDX microanalysis in the grainy areas suggests that this is the shell calcite. Indeed, five assays in different areas that had the same appearance gave an almost identical spectrum, always oxygen, carbon and a predominance of calcium.

The erosion of the outermost layer of the surface, which is dark in the images and formed by compact successive layers (presumably periostracum), exposes the inorganic part of the shell, the ostracum. The ostracum is lighter colored and grainy and it has a crystal texture. The effects are clear in sample 2, which is particularly affected by abrasion. One possible explanation for this erosion is that the impact of ultrasound waves and the process of cavitation harm the outer layers of the shell through erosion or abrasion. Ensminger and Stulen (2008) argue that some of the chemical and physical effects associated with high-intensity cavitation include production of OH (hydroxyl) and other ions, erosion of metal surfaces, disruption of aggregates, and other effects not producible by any other known means. It should also be taken into account that ultrasound waves increase the pressure and the temperature significantly during the cavitation process and this in turn could increase the effects of degradation (Suslick, 1989; Niemczewski, 2011; Santos et al., 2011; Wagterveld et al., 2011).

Pre-consolidation of sample 3 with TEOS-based consolidant does not avoid this degradation even though the degree of abrasion is lower. The consolidant does not spread out homogeneously and we did not observe penetration into the inorganic substrate. After cleaning, the consolidant appears in the form of isolated deposits. The siliceous nature of the deposit product helps to distinguish between the sample and the consolidant.

Using this method, we were unable to determine whether soil and dirt remain under the layer of consolidant. Certainly, the application of consolidant on the uncleaned specimen has the effect of consolidating any dirt. If the treatment had penetrated into the shell - which unfortunately did not occur in our study - , cleaning of the mollusk shell surface would have been possible. The precipitation of silicate deposits on the surface shell probably occurred during the polymerization process of consolidant, in which case the reaction would have occurred before the ultrasound bath. Öztürk (1992) reported that the drawbacks of the siliceous consolidants are insufficient penetration and formation of shallow and hard surface crusts, formation of soluble salts as by-products in the consolidation reaction, and growth of precipitated crystals.

The poor effectiveness of consolidation may also be due to errors in application, difficulty concerning the penetration of consolidant into the compact crystalline structure, and/or the size of pores of the periostracum (Rodriguez-Maribona and Cano, 2000). Penetration could be improved if the consolidant was applied in a vacuum. The application of TEOS-based consolidant in mollusk shells has not been tested previously. Further investigation is thus needed regarding the distribution and penetration of the consolidant. Different analytical techniques, such as the observation of a cross section, should be applied.

Our preliminary results are illustrative but not representative due to the small sampling size. A future, systematic study is needed to obtain a clear picture of the usefulness of the proposed methods.

To accurately determine the level of degradation caused by ultrasound, it is necessary to carry out further microscopic observations with samples of diverse characteristics and controls for more variables. These observations should be done on the same sample before and after the treatment to establish the effects of duration and intensity of exposure to ultrasonic waves. It would also be interesting to conduct a temporal survey to detect the long-term consequences of cleaning.

CONCLUSIONS

SEM observation highlights damage on mollusk shells caused by ultrasound cleaning that are not detected by stereomicroscopic observation. Thus, we recommend checking the resistance and the physical properties of the specimens in depth before carrying out any cleaning of this type. In spite of the evidence of microscopic degradation, this alteration does not affect the use of these samples for comparative purposes in identification campaigns. The pending question is how this kind of deterioration lowers the suitability for other scientific uses, and what could happen in the long term. Even though this is a preliminary study, we believe the findings are a starting point for further research on the effects of conservation treatment of natural history collections with ultrasound, particularly on mollusk specimens.

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REFERENCES CITED

AIC. 1994. Code of Ethics and Guidelines for Practice. The American Institute for Conservation of Historic & Artistic Works, Washington, DC, USA, 10 pp.

Araujo, R., G. Delvene, and M. Munt. 2014. Presence of organic layers in shells of fossil and recent Unionoida (Bivalvia) and their implications. Journal of Molluscan Studies 80:74–83.

Caracanhas Cavallari, D., R. Brincalepe Salvador, and B. Rodrigues da Cunha. 2014. Dangers to malacological collections: Bynesian decay and pyrite decay. Collection Forum 28:35–46.

Child, R. E., and C. Buttler. 1996. Cracking molluscan shells. Natural History Conservation 8–10.

Cortadellas, N., E. Fernández, and A. Garcia. 2012. Biomedical and biological applications of Scanning Electron Microscopy. Handbook of Instrumental Techniques for Materials, Chemical and Biosciences Research. Handbook of Instrumental Techniques for Materials, Chemical and Biosciences Research. Centres Científics I Tecnològics, Universitat de Barcelona 3:231–240.

Danehey, C., G. S. Wheeler, and S.-C. H. Su. 1992. The influence of quartz and calcite on the polymerization of methyl-trimethoxysilane; pp. 1043–1052 in J. Delgado Rodrigues, F. Henriques, and F. Telmo Jeremias (eds.), Proceedings of the 7th International Congress on Deterioration and Conservation of Stone: held in Lisbon, Portugal, 15-18 June 1992. Laboratório Nacional de Engenharia Civil.

De Prins, R. 2007. Détérioration des collections de coquilles. Causes, conséquences et traitement. Gloria Maris. Belgian Society for Conchology 2:43–56.

ECCO. 2003. E.C.C.O. Professional Guidelines (II). European Confederation of Conservator-Restorers' Organisations A.I.S.B.L., Brussels, Belgium, 4 pp.

Ensminger, D., and F. B. Stulen. 2008. Ultrasonics: Data, Equations and Their Practical Uses. CRC Press, Boca Raton, USA, 510 pp.

Furuhashi, T., A. Beran, M. Blazso, Z. Czegeny, C. Schwarzinger, and G. Steiner. 2009. Pyrolysis GC/MS and IR Spectroscopy in chitin analysis of molluscan shells. Bioscience, Biotechnology, and Biochemistry 73:93–103.

Geist, J., H. Wunderlich, and R. Kuehn. 2008. Use of mollusc shells for DNA-based molecular analyses. Journal of Molluscan Studies 74:337–343.

Harper, E. M. 1997. The molluscan periostracum: an important constraint in bivalve evolution. Palaeontology 40:71–98.

ICOM-CC. 2006. Código de deontología para Museos ICOM-CC. Available at http://www.icomce.org/recursos/File/Permanentes/Documentos%20ICOM/codigo%20deont%20nueva%20version%20enero07.pdf (December 2015)

Juanes Barber, D., and C. Martín de Hijas Díez. 2008. Aplicaciones de la microscopía óptica y electrónica de barrido; pp. 68–80 in La Ciencia y el Arte. Secretaría General Técnica, Subdirección General de Publicaciones, Información y Documentación, Ministerio de Cultura, Madrid, Spain.

Korniushin, A. V. 2000. Review of the Family Sphaeriidae (Mollusca: Bivalvia) of Australia, With the Description of Four New Species. Records of the Australian Museum 52:41–102.

Kuban, G. 2004. Fossil Preparation: Introduction to Fossil Collecting. K-Paleo Place. Available at http://paleo.cc/kpaleo/fossprep.htm (September, 2015).

Leonel, R. M. V., D. T. de Moraes, and S. G. B. C. Lopes. 2006. A new method of analysis of the periostracum in pallets of *Bankia* Gray, 1842 (Bivalvia: Teredinidae). Journal of Molluscan Studies 72:117–117.

Meyer, H. W., and D. M. Smith. 2008. Paleontology of the Upper Eocene Florissant Formation, Colorado. Geological Society of America, Boulder, USA, 192 pp.

Morton, J. 2006. The effect of relative humidity on mollusc periostracum and the use of coatings to prevent loss. Collection Forum 20:67–82.

Niemczewski, B. 2007. Observations of water cavitation intensity under practical ultrasonic cleaning conditions. Ultrasonics Sonochemistry 14:13–18.

Öztürk, I. 1992. Alkoxysilanes Consolidation of Stone and Earthen Building Materials. Master Thesis, University of Pennsylvania, Philadelphia, USA, 216 pp.

de Paula, S. M., and M. Silveira. 2009. Studies on molluscan shells: Contributions from microscopic and analytical methods. Micron 40:669–690.

Price, C. A. 1996. Stone Conservation: An Overview of Current Research. Getty Conservation Institute, Los Angeles, USA, 176 pp.

Rodriguez-Maribona, I., and M. Cano. 2000. Consolidación de la piedra monumental. Arte Y Cemento, Rehabilitación 112–117.

Ruedrich, J., T. Weiss, and S. Siegesmund. 2002. Thermal behaviour of weathered and consolidated marbles. Geological Society, London, Special Publications 205:255–271.

Santos, R., P. Ceulemans, D. François, and T. Van Gerven. 2011. Ultrasound-enhanced mineral carbonation. Proceedings of the 50th Conference of Metallurgists and the 6th International Symposium on Waste Recycling in Mineral and Metallurgical Industries, Montreal, Canada 108–116.

Smith, A. G. 1962. Notes on cleaning mollusks. Veliger 4:216.

Suslick, K. S. 1989. The Chemical Effects of Ultrasound. Scientific American 260:80–86.

Tennent, N. H., and T. Baird. 1985. The deterioration of Mollusca collections: identification of shell efflorescence. Studies in Conservation 30:73–85.

Wagterveld, R. M., L. Boels, M. J. Mayer, and G. J. Witkamp. 2011. Visualization of acoustic cavitation effects on suspended calcite crystals. Ultrasonics Sonochemistry 18:216–225.

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STUDY ON THE PHYSICAL-MECHANICAL COMPORTMENT IN SIX GAP FILLERS FOR FOSSIL REINTEGRATION

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ABSTRACT

Fossil reintegration is an unreliable field regarding intervention criteria and materials used according to the characteristics and requirements of specimens.
Generalized use of epoxy fillers in different kinds of gaps suggest that an in-depth study on more reversible gap fillers for small to medium fossils is necessary.
This paper investigates the physical-mechanical comportment of six gap fillers of three different families of resins: vinyl, acrylic and epoxy.
Samples have been tested according to their working properties, aging properties, and affinity with paleontological materials. A physical-mechanical characterization has been done to gap fillers according to different parameters. Moreover, accelerated artificial aging tests have been done in all samples. After that, changes have been quantified with several analysis techniques.

Keywords: fossil gap filler; paleontological conservation; reintegration; preparation

RESUMO [in Portuguese]

A reintegração dos fósseis é um domínio não fiável se tivermos em conta os critérios de intervenção e materiais usados de acordo com as características e requisitos dos espécimes.
O uso generalizado da não-reversível epoxy para preencher diferentes tamanhos de espaços em fracturas é indicador de que mais investigação é necessária para se encontrarem colas de preenchimento reversíveis para fracturas em fósseis de tamanho pequeno a médio.
Este projecto estuda os comportamentos físico-mecânicos de seis tipos de colas de preenchimento de três famílias diferentes de resinas: vinil, acrílico e epoxy.
Foram testadas amostras considerando as suas propriedades de manuseamento, envelhecimento e afinidade com materiais paleontológicos. Foi feita uma caracterização físico-mecânica das diferentes colas de preenchimento de acordo com vários parâmetros. Mais acresce testes de envelhecimento artificial acelerado foram feiros em todas as amostras. Depois foram quantificadas as alterações das propriedades das colas com várias análises técnicas.

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INTRODUCTION

Criteria in paleontological conservation and paleontological reintegration of specimens are currently well-established amongst professionals. However, these criteria are not always respected.

Moreover, fossil reintegration is a little investigated and referenced field at this moment in Spain; even though the collection, classification, study and preparation of fossil specimens is already commonly applied (Baeza Chico et al., 2009).

As a consequence of historical paleontological excavations, fossil reintegration has been realized by professionals from different fields such as paleontologists, archaeologists, traditional preparators, museum workers, restorators or fossil owners (Thornton, 1998). All these different approaches have challenged criteria and methodologies (consciously or un-consciously) in the conservation of specimens.

Heterogeneity of materials that have been traditionally used as fillers in fossil reintegration show that more research is needed regarding methods and materials (Martínez Riera, 2015). Moreover, generalized use of epoxy resins as fillers raises the necessity to search for alternative fillers with a higher reversibility for its use on medium to small fossils. This is because generalized use of epoxy resins for reintegration shows serious problems in reversibility when applied on specimens, and might even cause structural damage. Therefore, it is necessary to establish criteria and unify the intervention processes of epoxy resins as fillers.

OBJECTIVES

Despite the use of epoxy resins in fossil re-construction in Spain as well as other countries, there are no specific studies that evaluate the comportment of these resins. It is necessary to evaluate what advantages and disadvantages different resins provide when used, and what possible damage may be caused in short or longer term to specimens.

There are already some studies from abroad on finding alternative fillers, such as temporary gap filling (Davidson, 2009) or reversible fillers (Haugrud and Compton, 2008). It is vital to propose alternatives in order to expand the range of options for fossil reintegration so professionals could evaluate the most suitable filler.

Under these premises, the main objective of this study is to carry out a comparison between different types of fillers with different kinds of synthetic resins of higher reversibility for small to medium fossils.

METHODOLOGY

Preparation of samples: components selection and proportions

Six different fillers from three different groups of synthetic resins have been tested: vinyl resins, polyvinyl acetate (PVAs) Rayt Standard® (Koob, 1998) and Mowital B60HH® (López Amador and Pellejero, 2007); acrylic resin, Paraloid B72® (Aberasturi Rodríguez et al., 2009); epoxy resin, Epo 150® (Lastras Pérez et al., 2007) and Araldit SV427®. Six formulas are based on polymers that have been previously used in paleontological conservation or have been suggested by other authors (Loew Craft and Solz, 1998). Powdered fossil matrix and glass microballs (0,50µ) have been added into the mixtures in several proportions to create the samples.

Thirty-two compositions (Martínez Riera, 2015) have been created before choosing the last six fillers. Four samples have been elaborated with each filler. One sample has been used as "control sample" and three of them have been tested. Measures of every sample are 35 x 35 x 10 mm. The six gap fillers are the following (see also Table 1):

- PVAs + powdered fossil matrix: filler nº1 (PV). Filler based on PVAs that originate from traditional PVAs fillers used in fossil reintegration (Koob, 1998).
- PVAs + powdered fossil matrix + glass microballs: filler nº2 (PM). This composition has been realized from filler nº1. Glass microballs have been added to the mixture to improve its physical-mechanical properties and control humidity.
- Vinylbutiral polymer + powdered fossil matrix + glass microballs: filler nº3 (M). This filler is made from the use of Mowital B60HH® in the consolidation of specimens and archeological reintegration.
- Ethylmetacrylate polymer + powdered fossil matrix + glass microballs: Filler nº4 (P). Paraloid B72® is frequently used as consolidant in paleontological conservation

(Aberasturi Rodríguez et al., 2009). Paraloid B72® is used as well in fillers with glass microballs for fossil and archeological reintegration (Larkin and Makridou, 1999). Fillers with Paraloid B72® and glass microballs have been used as reference to elaborate new fillers adding powdered fossil matrix. A proportion that has been used was 25% Paraloid B72® in acetone (Larkin and Makridou, 1999). Other authors note that the best results are obtained with solutions between 25-50% (Fox, 2001).

- Epo 150® + powdered fossil matrix: filler nº5 (E). This filler has been used in different proportions in reintegration of archeological specimens (Lastras Pérez et al., 2007). Commercial fillers based on epoxy resin are frequently used, therefore we decided to test the properties of one such simple commercial epoxy resins.
- Araldit SV427®: filler nº6 (A). Another commercial epoxy resin has been chosen in order to compare the properties between a commercial epoxy resin to other fillers used in this study.

Table 1- Summary of fillers and components.

Nº / Ref.	**Proportions (% mass)**
Nº1 / PV	Rayt Standard® 95% water (55%) + fossil matrix (45%)
Nº2 / PM	Rayt Standard® 95% water (40%) + glass microballs (30%) + fossil matrix (30%)
Nº3 / M	Mowital B60HH® 10% ethanol (16%) + glass microballs (42%) + fossil matrix (42%)
Nº4 / P	Paraloid B72® 25% acetone (20%) + glass microballs (40%) + fossil matrix (40%)
Nº5 / E	Epo 150® (25%) + fossil matrix (75%)
Nº6 / A	Araltdit SV427® (commercial product)

Techniques and technical equipment used for analysis

Three analyzing techniques have been applied before and after chemical tests; electronic precision scale, optical microscopy, image analysis and spectrometry-colorimetry.

Electronic Precision Scale

An electronic precision scale has been used, model GRAM BH-30024 (maximum weight 300g - 0.01 g resolution). The scale has been used to take measurements and to weigh samples before and after tests in order to keep mass changes under control after accelerated artificial aging tests (Màs Barberà, 2008).

Spectrometry-Colorimetry

Spectrometry-colorimetry is a non-destructive analysis technique (Martínez Bazán, 2007). A Minolta CM-2600d Spectrophotometer has been used to get chromatic coordinates. Standard illuminant CIE type D56 (sunlight, 6500° K color temperature) and standard observer (10º) have been chosen as measurement conditions. Data were taken with specular component included (SCI), which minimizes the influence of conditions in the surface of the sample. Light source consists of three pulsed xenon lamps. Integrating sphere (52 mm Ø) is coated with $BaSO_4$. Spectrophotometer wavelength range is between 360 and 740 nm (wavelength pitch 10nm). Its reflectance range is 0 to 175% with 0.01% display resolution. Repeatability has a standard deviation of 0.1% in spectral reflectance, and chromaticity value ΔE * ab within 0.04 (ICD 76).

Optical microscopy and image analysis

The surface of the samples has been observed before and after accelerated artificial aging tests to determine changes. Images have been taken by stereomicroscope and binocular tubes. The equipment is the model Leica MZ APO25 with fiber optic illuminators and resolution from 8x to 80x. Photographs were taken by a camera adapter system with a digital camera. Images were processed by Leica Microsystems software. The photographs were taken with zoom 8x and 16x in every sample although 50x have been used in some samples after SO_2 saturated atmosphere accelerated artificial aging test.

Tests performed

Several tests have been done on every sample to determine different characteristics of the fillers. On the one hand a physical-mechanical test has been done: physical-mechanical characterization of working properties. On the other hand three chemical tests have been made simulating extreme environmental conditions: ultraviolet radiation accelerated artificial aging test, SO_2 saturated atmosphere accelerated artificial aging test and humidity and temperature accelerated artificial aging test.

Physical-mechanical test

Physical-mechanical characterization test of working properties. Physical-mechanical characterization by working properties of the fillers has been tested through the physical-mechanical test. This tests the parameters that a good filler must have (Fox, 2001; Lastras Pérez, 2007). The parameters are tested through the evaluation of properties of every sample (Loew Craft and Solz, 1998) by means of mechanical and physical procedures.

- Reversibility: depends on the solubility of the resin used in the composition of the filler and on the kind of solvent used to prepare the resin. Mechanical tools have been used to perform this test.
- Compatibility: compatibility of resins with specimens has been tested. Filler components have been chosen according to previous paleontological interventions and scientific studies in conservation that have shown good results.
- Structural resistance: structural resistance has been tested in each sample regarding their resistance after the drying process.
- Preparation: it is tested how simple and fast the preparation of every filler can be.
- Application: the way of application, molding, modelling and injection is evaluated.
- Drying time: time of drying is tested using the following parameters: 24 h, slow; less than 24 h, good; less than 1 hour, fast.
- Adhesion: the adhesive power of fillers.
- Volume change and cracking: observation of the volume change and cracking during cure time of samples.
- Leveling and polishing: every sample has been tested working with different tools such as a scalpel and mechanical tools of polishing (rotary tool, carborundum accessories).
- Color adjustment: color adjustment a secco has been evaluated after the drying process of the samples.
- Toxicity: depends on solvents and resins used. Companies must inform about it. It is really important to minimize toxicity for the sake of the conservators�može health and the environment.

Chemical tests

Ultraviolet (UV) radiation accelerated artificial aging test. Through the ultraviolet radiation accelerated artificial aging tests it is possible to determine what the reaction is of fillers to solar radiation and lighting inside museum rooms. UV irradiation is a cumulative degradation process in artifacts, and particularly in paleontological specimens. Light and UV exposition are registered in museum rooms by means of data loggers, and controlled by UV filters. Nevertheless, keeping UV conditions under control outside museums is more complicated because climate agents are more aggressive and variable in urban or natural environments.

Illumination conditions are recommended to specimens between 290-400 nm; direct illumination and natural light have to be avoided in museum rooms (Howie, 1979). UV radiation accelerated artificial aging tests were made to simulate environmental exhibition conditions in museum rooms. Samples have been exposed to alternating cycles of UV radiation (351 nm) for 800 hours in a QUV-BASIC QPANEL accelerated weathering tester.

Humidity and temperature accelerated artificial aging test. Relative humidity (RH) and temperature affect specimens and fillers contraction and expansion. Moreover, color is changed as well. That is the reason why physical and chemical properties of fillers are affected (Howie, 1979). In addition, saline efflorescence appears after relative humidity and temperature fluctuations in paleontological specimens, which can cause severe damage in materials (Baeza Chico and Menéndez, 2005).

Through humidity and temperature accelerated artificial aging test, extreme climatic conditions are simulated to test the properties of fillers. The test has been done in a climatic chamber DYCOMETAL MODEL CCK- 25/300 in 24 hours cycles with 60 ºC and 75% RH (cycle 1) and a

20 ºC and 20% RH (cycle 2) for one month. According to some authors, relative humidity is recommended to be between 30-60% (Baeza Chico and Menéndez, 2005) and temperatures are suggested around 23 ºC to storage (Leiggi and May, 2005).

SO_2 saturated atmosphere accelerated artificial aging test. It is possible to evaluate the effect of atmospheric agents in samples using the SO_2 saturated atmosphere accelerated artificial aging test. Resistance to sulfur dioxide has been tested because it is considered one of the most corrosive and common gases in the atmosphere. Sulfur dioxide comes from natural emissions such as volcanoes or artificial emissions (Gisbert Aguilar and Marín Chaves, 2001).

Chemicals contained in the atmosphere have accelerated the deterioration process in the last years because of the increase of industrial production and urban areas. It has become one of the most difficult alterations to keep under control. It is responsible of degradation processes such as rock sulfation (Gisbert Aguilar and Marín Chaves, 2001) and damages in paleontological specimens in museums (Howie, 1979). The test has been done using a VCK-300 MODEL DYCOMETAL chamber through the Kesternich EXPLICAR test according to DIN 50018 (SO_2 corrosion) with 4 cycles of duration.

RESULTS

Physical-mechanical characterization of working properties test

Different parameters have been tested to determine the best qualities of the materials (Fox, 2001; Lastras Pérez, 2007), according to their working properties (Loew Craft and Solz, 1998). Classification of each filler in every parameter of this test consists of four levels: very good/good/bad/no results.

- **Reversibility:** reversibility tests have been performed using immersion for 30 minutes in water, ethanol and acetone.

  Filler nº4 dissolves very well in ethanol while the solution is good and progressive in nº3. PVAs show only a light softening under ethanol immersion, whereas fillers based on epoxy resin are not reversible by ethanol immersion (Figure 1).

  Filler nº4 quickly dissolved in acetone. Filler nº3 has good softening and lost its consistency. Fillers nº1 and nº2 increase in volume, which makes them easier to remove with a scalpel. Fillers nº5 and nº6 do not show changes.

  Fillers are not reversible in water; only fillers based on PVAs show a slight softening, which makes them more pliable for a scalpel.

  All fillers can be removed by mechanical means. Fillers nº3 and nº4 are easy to remove by scalpels or other mechanical tools. In order to minimize damage, ethanol or acetone can be used to dissolve the filler. Nº5 and nº6 are not reversible because they are epoxy resins. Even though they can be removed by mechanical means, specimens can be affected by physical stress when epoxy resins are removed.

- **Compatibility:** PVAs fillers are used as consolidants and adhesives in fossils due to their flexibility and structural resistance (López Amador and Pellejero, 2007). Filler nº1 has been used at 95% dissolution in water. Samples with higher proportions show high water retention rates, despite the actual proportions of water being very low. Therefore, fillers based on resins that are dissolved in water are not recommended because humidity can affect the fossil. The use of fossil matrix is a guarantee of fossil compatibility because they have same composition.

  The same proportion as in filler nº1 has been used in filler nº2 but adding glass microballs. These have been used to reduce and control humidity. Therefore, a 55% of Rayt Standard at 95% in deionized water has been used, whereas the 45% filler is difused with glass microballs. This reduced the humidity, however, it is still considered high.

  Vinylbutiral polymer is used as a consolidant in fossils because it is transparent and flexible (López Amador and Pellejero, 2007). Ethanol has been used in this test, such that no water is added to the specimens.

  Paraloid B72® has already been tested on many different materials in order to evaluate its stability and compatibility. It is also used in many interventions in paleontological conservation (Romero et al., 2007; González Santiago et al., 2008). Using Paraloid B72® dissolved in acetone avoids the need for water and keeps solvent impregnation under control due to acetone volatility.

  Despite the recommendation of Epo 150® as a filler for stone, it could deform small fossils because of the thermal reaction that is

Figure 1 – Samples after the physical-mechanical characterization of working properties test, which shows reversibility after 30 minutes in ethanol.

produced during the catalysis in a non-reversible way.

Araldit SV427® is a filler used in wood reintegration and although it is used in paleontological conservation as well, the compatibility with fossil material has not been studied.

- **Structural resistance:** Filler nº1 has been used with lower adhesive volumes than fossil matrix, otherwise samples are too elastic and soft due to an excessive use of resin. Filler shape is maintained after applying manual strength.

Structural resistance has been improved in filler nº2 because PVAs levels have been reduced due to the use of glass microballs, therefore the mixture is harder and more resistant to manual strength.

Low resin concentrations in ethanol have been used to prepare the filler nº3, in order to avoid high viscosity, glossy surface and excessive elasticity. Filler nº3 shows enough hardness to resist manual strength.

High resin concentrations have been avoided in filler nº4 because of the positive properties obtained using a mixture of fossil matrix and glass microballs instead of dissolution of the resin. Despite using high levels of resin, fillers of this concentration showed a good plasticity. Using too much resin makes fillers softer and too elastic. When resin concentrations are too low, adhesivity is reduced and fillers are useless. A balanced filler has been obatined, which is elastic enough and resistant to manual strength.

Epo 150® has high resistance properties, therefore it should only be used in very resistant specimens. Epo 150® could add more weight to the specimen so it is not recommended for large fossils. Therefore, the handling of fossils could be more difficult. It is neither recommended for medium nor small fossil bones because it could cause deformations.

Araldit SV427® also has a high structural resistance, and is recommended for big specimens. With the exclusion of Epo 150®, Araldit SV427® is lighter than the other epoxy fillers.

- **Preparation:** Necessary tools for preparation are a measuring cap, a scale and a spatula.

  Preparation of PVAs fillers is easy and fast. Filler nº3 is also fast to prepare when it is dissolved immediately in ethanol.

  Filler nº4 requires dissolution of the resin in acetone at least 24 h prior to use (Andrew, 2009). Paraloid B72® solution can be used for preparation instantly.

  To prepare filler nº5, both components of the resin need to be mixed (resin and catalyst). The mixture can be used immediately and the preparation is fast and easy.

  Araldit SV427® is prepared by mixing two components of the resin in 1:1 in mass. Preparation is easy.

- **Application:** PVAs fillers have a pasty consistency. Application can be done by molding. They have the capacity to be molded as well as to record details by taking casts. They are not recommended for injection because of the particle size and consistency. Glass microballs improve detailed casting because particle size is reduced, although viscosity is also too high for injection.

  Fillers nº3 and nº4 are thick mixtures so they can be molded while drying. These fillers allow a higher detailed casting but cannot be injected.

  Filler nº4 produces a film on the surface after being applied, which makes it more difficult to work with. This reaction can be solved by changing the surface tension of the filler by using some drops of methanol or ethanol while preparing the filler (Lastras Pérez, 2007).

  Filler nº5 has a pasty consistency. It can be modelled and shaped with a good ability to record details. It is not suitable for injection because of its high viscosity.

  Araldit SV427® is doughy, it is easy to shape and has a very high precision record when used for molding. A smoother surface of the gap filled before the filler is dried is obtained when wetting the spatula in acetone or water.

- **Drying time:** PVAs fillers have similar properties during drying period although drying time in PVAs fillers with glass microballs is shorter. Total drying time is slow, over 24 hours, when we allowed natural drying, although this depends on the climate conditions. If the drying time is accelerated through artificial heating, a stratification in the samples appears, making drying of internal parts of the samples more difficult. When samples are used by molding, the drying is very slow and irregular, which is increased by using silicon molds that isolate the internal part from the environment (Figure 2). Slow drying results in high humidity for a long time, so that PVAs fillers cannot be recommended for application on fossil bones.

  Drying time in filler nº3 is good. This filler allows time enough to have a good application and work it in. Drying time depends on solvent volatility, although this is conditioned by climate conditions.

  The drying time of filler nº4 is good. Filler nº4 has good working properties together

Figure 2 – Detail of strata drying in PVAs gap fillers compared to Paraloid B72® gap fillers.

with drying time, and can be kept under control by adding other solvents with lower volatility such as methanol or ethanol (Lastras Pérez, 2007).

Drying time in filler nº5 is slow because it depends on the catalysis resin process (24 hr at least). The same happens to Araldit SV427®. Time could be variable depending on atmospheric conditions.

- **Adhesion**: PVAs fillers show very good adhesive properties. They show high resistance and elasticity (López Amador and Pellejero, 2007). Mowital B60HH® and Paraloid B72® also display good adhesive properties and good elasticity. Paraloid B72® at 20% concentration gives fillers good adhesive properties to medium specimens. However, epoxy fillers show high adhesive power and are very resistant so they are recommended to heavy and big fossils.
- **Volume change and cracking:** PVAs fillers have similar properties related to volume change during the drying process. Volume change is medium to high, although the humidity on the mixture preparation process has been controlled by adding glass microballs (Figure 3). When water levels are higher, the volumetric change is higher too, however, cracking of the fillers decreases, which gives better cohesion to the mixture. Larger amounts of glass microballs therefore avoids cracking of the filler and reduces the change in volume. Volume change in fillers nº3, 4, 5 and 6 is virtually null or imperceptible to the human eye. No cracking of the surface has been observed either.
- **Leveling and polishing:** PVAs fillers, due to their plastic surface, can be leveled cutting the surface with a scalpel, although the surface will be irregular and it will be difficult to have a smooth surface. Sanding or grinding, either by manual means with sandpaper, or by mechanical means with a micromotor does not work, because fillers have a plastic surface. Fillers nº3 and 4 have similar working properties. Mechanical tools (scalpel, rotatory tool) can be used on the surface. Surface sanding is easy by means of sandpaper or polishing with electrical tools. The surface can be softened to work easier with proper solvents.

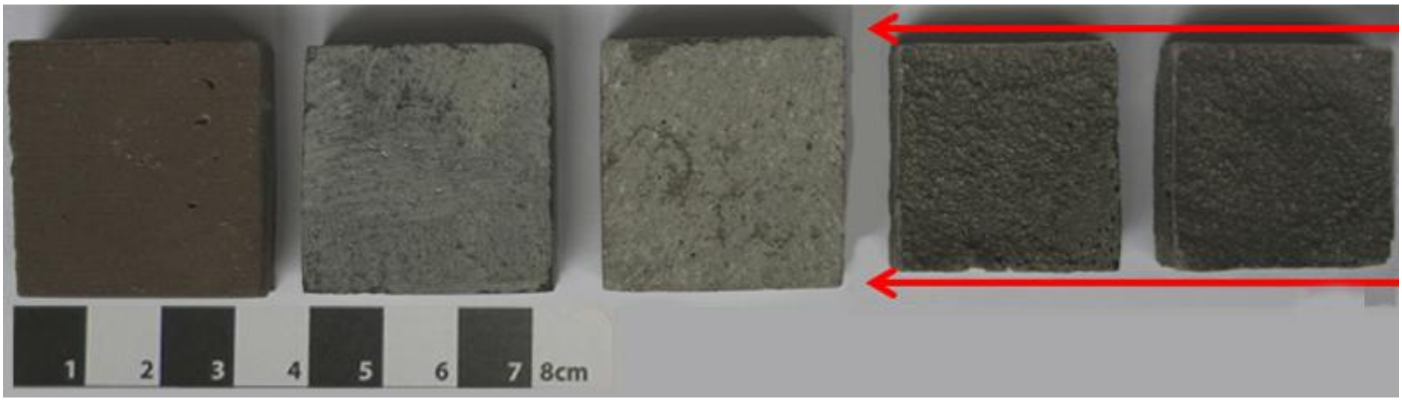


Figure 3 – Volume loss in PVAs gap fillers compared to other fillers.

Filler nº5 is very difficult to level with a scalpel because the filler is too hard. Filler nº5 can be modeled and polished with mechanical tools, although this could produce mechanical stress to the specimens. Levelling is recommended before drying. Araldit SV247® can be carved with a scalpel or other mechanical tools. This filler can be sanded with sandpaper or a rotatory tool.

- **Color adjustment:** PVAs fillers do not allow retouching with watercolor or glazing with water due to their plastic surface. However, adjustments can be made through other acrylic-based paint or other solvents. Other fillers allow color retouching with any water-based paint or other solvents.
- **Toxicity:** PVAs Rayt Standard® is a non-harmful and non-hazardous product. Furthermore, the common solvent used is deionized water, which is a harmless product. Fillers nº3 and 4 will be more toxic due to the use of ethanol and acetone as solvents. The toxicity of fillers based on Epo 150® and Araldit SV427® is determined by the composition of the resins, which must be listed by the brand.

All fillers have a good leveling, polishing and color reintegration (Figures 4 and 5) except PVAs fillers, due to their plastic surface. They cannot be colored with watercolors. PVAs fillers experience a huge change in their volume compared to other fillers. Drying is regular in every gap filler excepting PVAs fillers because they show a stratified drying. Epoxy fillers display great adhesion power.

Ultraviolet radiation accelerated artificial aging test

General rates of mass loss have been registered between 0,43 g and 0,10 g. Loss in mass is probably due to the loss of humidity of fillers during the test. Filler nº5 shows the best properties with any variation. Loss in mass could be related to changes of physical-mechanical properties after long expositions to UV radiation (Table 2).

There are no relevant changes in the surface of the samples after comparing the optic microscopy images before and after the UV radiation accelerated artificial aging test.

There are significant changes in colorimetric coordinates. Colorimetric analysis (Figure 4) shows visible changes ΔL* (4,56) and ΔAEab* (5,01) of filler nº4. Filler nº3 reveals equal deviations although rates are lower. PVAs fillers present similar results, although rates are

Table 2 - Rates of mass loss: Ultraviolet radiation accelerated artificial aging test (mass in g).

Samples for Ultraviolet radiation accelerated artificial aging test (mass in g)									
FILLER	**Nº OF FILLER**								**AVERAGE CHANGES**
	1		**2**		**3**		**4**		
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	
PV	14,1		12,9	12,8	15,7	15,5	14,7	14,5	-0,17
PM	18,3		18,8	18,4	16,1	15,7	16,5	16	-0,43
P	20,9		21,3	21,2	20,7	20,6	18,7	18,6	-0,10
M	17,8		16,4	16,2	21,3	21,1	21	20,9	-0,17
E	20,3		21,3	21,3	21	21	25,7	25,7	0,00
A	10,31		7,6	7,5	9,7	9,6	8,6	8,5	-0,10

bigger in ΔL* (8,20) and ΔAEab* (9,68) in the gap filler with glass microballs. Epo 150® filler has the most stable rates with visible changes in ΔL* (2,29) and ΔAEab* (3,75). The most unstable filler is Araldit SV427®, which shows visible changes in all the parameters.

There are relevant visible changes in chroma (C*) rates in fillers based on PVAs and Araldit SV427®. Araldit SV427® shows in ΔC* a maximum of -8,82 units CIELAB. There are also visible changes in filler nº4 (-2,05) although changes are not as important as in Araldit SV427®. All fillers change chroma from weak (before test) to greyish.

The Araldit SV427® reveals visible changes in color tone (h*); the filler changes from orange tone (56,30) to orange-red (49,76).

Paraloid B72® and PVAs samples do not show changes regarding color tone (h*). Tone is orange-yellow before and after the test. Fillers nº3 and nº5 maintain also a stable tone yellow-orange. Fillers nº3 and nº5 reveal also a weak chroma (C*) without any visible changes.

There are visible changes only in Araldit SV427® on rate L*. Data conversion reveal that brightness has a medium level before ultraviolet radiation accelerated artificial aging test but it shows a light level after the test.

SO_2 saturated atmosphere accelerated artificial aging test

PVAs fillers do not show any relevant changes in mass (0-0,07 g) after this test, the same as epoxy gap fillers: Epo 150® (0 g) and Araldit SV427® (-0,03 g). Paraloid B72® (0,3 g) and Mowital B60HH® (0,9 g) fillers show the highest registered data of mass loss. This is probably related to a cohesion loss during the test and, consequently, the loss of material during the SO_2 saturated atmosphere accelerated artificial aging test (Table 3).

Relevant changes have been registered in colorimetric coordinates (Figure 5). The most stable are the gap fillers based on Paraloid B72® and Mowital B60HH®. They register visible changes in ΔAEab* of 3,61 and 2,8 respectively. Filler nº4 has changes in ΔL* of 3,21. Colorimetry analysis reveals the biggest change in the epoxy gap fillers. Araldit SV427® is the most variable in colorimetry with maximum rates in ΔAEab* of 21,78 and negative rate in Δa* of -7. Filler nº5 has high rates in ΔL* (17,65) and ΔAEab* (17,9). There are negative values in rates of Δb* (-2,81) and ΔC* (-2,81). Fillers based on PVAs show similar changes. PVAs fillers with glass microballs have higher values in ΔL* (9,41) and ΔAEab* (10,77), although PVAs fillers without glass microballs show higher rates in Δb* (-5,07) and ΔC* (-5,23).

The PVAs filler with glass microballs shows significative changes in chroma (C*; -5,23). Fillers nº3 and nº5 also show visible changes in chroma (C*) although they are lower and they change from weak chroma to greyish.

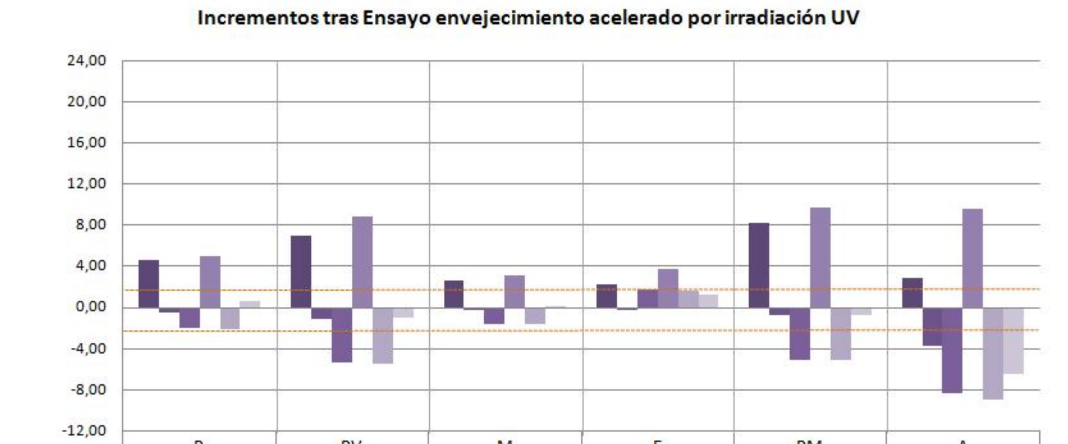
Araldit SV427® has an orange tone (h*) (57,81) that changes visibly to an orange-yellow tone (78,83) with Δh* of 21,01 units CIELAB. However, Paraloid B72® and PVA samples have orange-yellow tone. Fillers nº3 and nº5 have yellow-orange tone that are stable before and after the test.

Fillers based on Paraloid B72® and PVAs show medium brightness on rate L*. Fillers nº3 and nº5 are light. However, Araldit SV427® reveals brightness changes from medium to light.

Analyses using optic microscopy do not reveal general relevant changes before and after this test. However, there are changes in epoxy gap fillers: Araldite SV427® (Figure 6) and Epo 150® (Figure 6). These changes probably result from the resin characteristics, the fossil matrix used in the mixture or the products added during the SO_2 saturated atmosphere accelerated artificial aging test. In filler nº5 the test probably

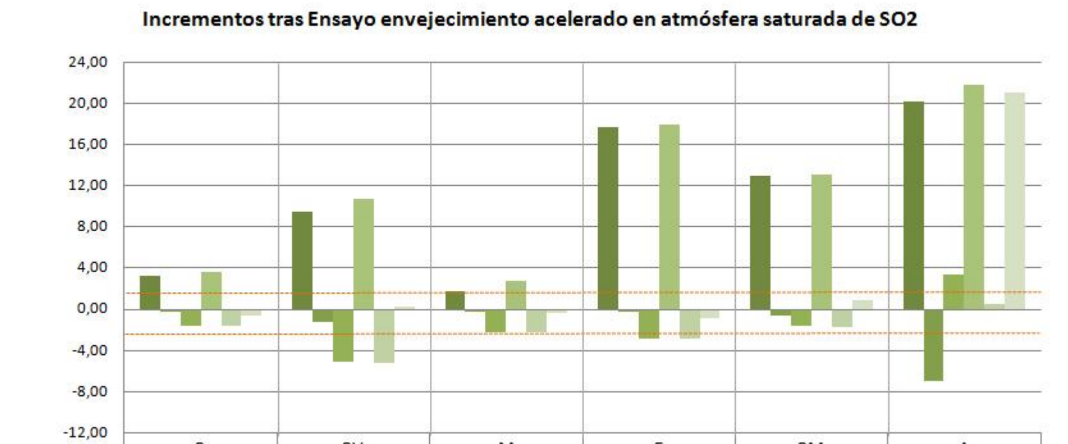
Table 3 - Rates of mass loss: SO_2 saturated atmosphere accelerated artificial aging test (mass in g).

Samples for SO_2 saturated atmosphere accelerated artificial aging test (mass in g)									
FILLER	**Nº OF FILLER**								**AVERAGE CHANGES**
	1		**2**		**3**		**4**		
	Before	**After**	Before	After	**Before**	**After**	**Before**	**After**	
PV	16,1	-	16,2	16,2			14,6	14,6	0,00
PM	15,9	-	19,4	19,4	15,9	15,7	16,7	16,7	-0,07
P	18,9	-	18,1	18,3	18,1	18,5	21	21,3	0,30
M	17,6	-	20,4	20	17,8	15,8	18,1	17,8	-0,90
E	21,5		25,5	25,5	25,6	25,6	21	21	0,00
A	9,3		9,7	9,7	7,9	7,8	8	8	-0,03



	P	PV	M	E	PM	A
ΔL*	4,56	7,03	2,66	2,29	8,20	2,89
Δa*	-0,54	-1,10	-0,23	-0,15	-0,78	-3,69
Δb*	-1,98	-5,31	-1,57	1,70	-5,05	-8,29
ΔAEab*	5,01	8,88	3,14	3,75	9,68	9,53
ΔC*	-2,05	-5,42	-1,59	1,69	-5,10	-8,89
Δh*	0,61	-0,99	0,02	1,20	-0,68	-6,51

Figure 4 – Graphic of increase in (SCI) ΔL*, Δa*, Δb*, ΔAEab*, ΔC*, Δh* during the ultraviolet radiation accelerated artificial aging test after processing colorimetric data.



	P	PV	M	E	PM	A
ΔL*	3,21	9,41	1,72	17,65	13,01	20,19
Δa*	-0,25	-1,28	-0,24	-0,09	-0,56	-7,00
Δb*	-1,59	-5,07	-2,19	-2,81	-1,65	3,38
ΔAEab*	3,61	10,77	2,80	17,90	13,12	21,78
ΔC*	-1,60	-5,23	-2,21	-2,81	-1,73	0,56
Δh*	-0,59	0,27	-0,35	-0,88	0,84	21,01

Figure 5 – Graphic of increases (SCI) ΔL*, Δa*, Δb*, ΔAEab*, ΔC*, Δh* after SO_2 saturated atmosphere accelerated artificial aging test after processing colorimetric data.

shows efflorescence salts (Figure 6). These presumed efflorescence salts appear also in Araldit SV427® as white spots on the surface (Figure 6). These spots need to be analyzed in further tests. Analysis using optic microscopy also shows that porosity has increased and new cracks have appeared in Mowital B60HH® fillers (Figure 7).

Humidity and temperature accelerated artificial aging test

PVAs fillers are really stable after the humidity and temperature accelerated artificial aging test. They register mass changes of 0 g and 0,07 g. Epo 150® filler appears stable after mass variation analysis, whereas Araldit SV427® has the highest mass change (0,27 g), which may be because of humidity absorption during the test. Filler nº4 (0,1 g) does not show any relevant changes. Filler nº3 (-0,03 g)

Table 4 - Rates of mass loss: Humidity and temperature accelerated artificial aging test (mass in g).

Samples for humidity and temperature accelerated artificial aging test (mass in g)									
FILLER	**Nº OF FILLER**								**AVERAGE CHANGES**
	1		**2**		**3**		**4**		
	Before	**After**	Before	After	**Before**	**After**	**Before**	**After**	
PV	17,1	-	13	13	13,9	13,9	15,4	15,4	0,00
PM	19,6	-	20,5	20,5	17	17,1	16,8	16,9	0,07
P	18,4	-	19,1	19,2	18,5	18,6	18,6	18,7	0,10
M	20,2	-	17,1	17	21,4	21,5	19,5	19,4	-0,03
E	27,2	-	22,5	22,5	22	22	26,9	26,9	0,00
A	8	-	10,1	10,4	9,8	10	9,2	9,5	0,27

shows a low mass loss, which can be considered irrelevant (Table 4).

Colorimetry analysis (Figure 8) shows important changes in several samples. Epo 150® is the most stable filler, there are no visible changes in its parameters. The biggest changes appear in Araldit SV427®, with negative visible registers in rates Δb* (-5,91), ΔC* (-5,82), and Δh* (-6,54) and positives in ΔAEab* of 6,42. PVAs fillers have similar results with almost identical quantities and figures (ΔAEab*: 6,62).

Filler nº4 is stable. It only reveals visible changes in ΔAEab* with 2,33. Filler nº3 has also a stable comportment similar to filler nº4. Rates have visible changes in ΔL* (2,08) and ΔAEab* (2,89).

There are visible changes in chroma (C*) in PVAs fillers and Araldit SV427® that change from weak chroma before the test to greyish with maximun ΔC* of -5,82 CIELAB units. In addition, in the Araldit SV427® sample, visible changes in tone (h*) go from orange (56,30) to orange-red (49,76).

Fillers nº1, nº2, and nº4 do not show visible changes. They maintain their orange-yellow tone (h*) before and after the test. The same happens with the fillers nº3 and nº5, which maintain tone (h*) in yellow-orange.

Fillers nº3, nº4, and nº5 do not reveal any visible changes in chroma (C*). They show weak chroma (C*) before and after the test.

L* rate reveals medium brightness in all fillers, however filler nº3 shows a light rate.

Optical microscopy image analysis does not reveal any change on the surface of the samples tested before and after humidity and temperature accelerated artificial aging test.

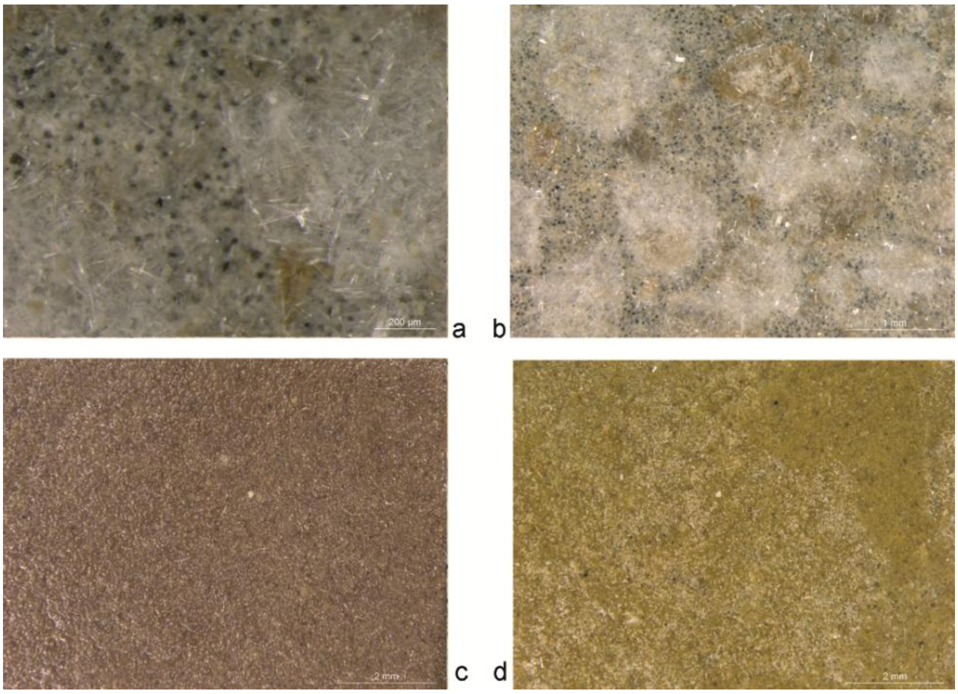


Figure 6 - A,B) (x16) possible salt efflorescence in Epo150® filler after SO_2 saturated atmosphere accelerated artificial aging test. C,D) Araldit SV427® before and after SO_2 saturated atmosphere accelerated artificial aging test where what seems to be salt efflorescence appears in the image taken after the test.

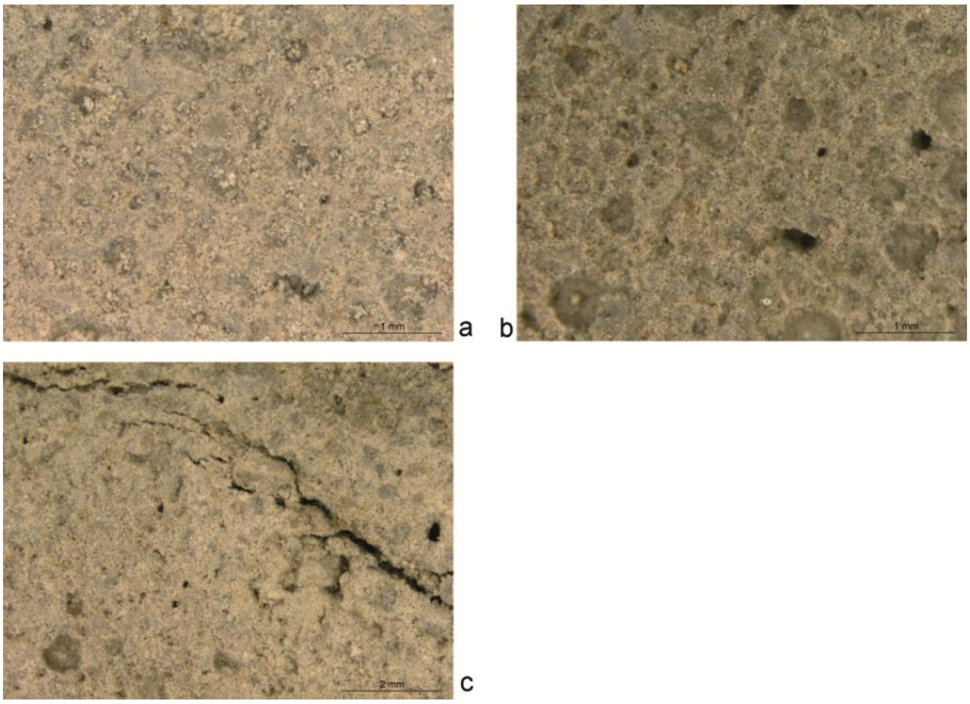
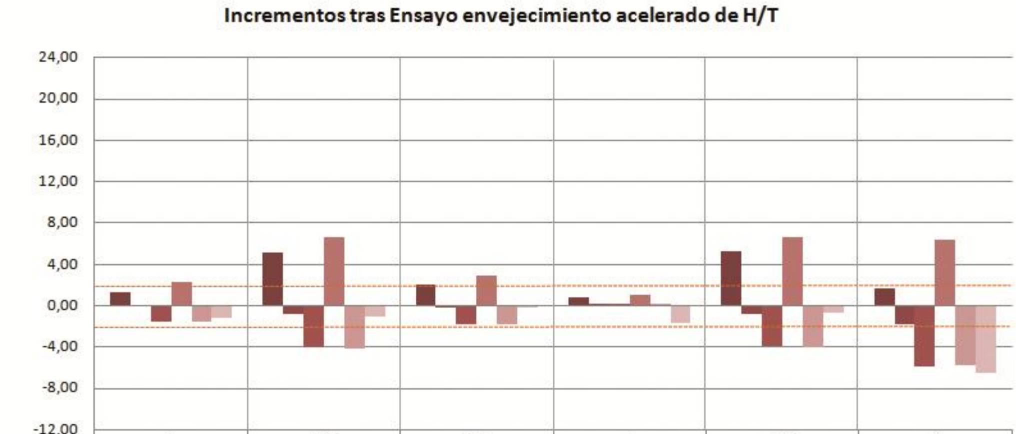


Figure 7 - A) (16x) shows the sample before the test. B,C) higher porosity and cracks after SO_2 saturated atmosphere accelerated artificial aging test in the Mowital B60HH® filler.



	P	PV	M	E	PM	A
ΔL*	1,33	5,15	2,08	0,76	5,22	1,72
Δa*	-0,12	-0,75	-0,20	0,22	-0,77	-1,81
Δb*	-1,60	-4,08	-1,81	0,11	-3,96	-5,91
ΔAEab*	2,33	6,62	2,89	1,10	6,62	6,42
ΔC*	-1,58	-4,14	-1,82	0,12	-4,04	-5,82
Δh*	-1,22	-1,07	-0,22	-1,62	-0,66	-6,54

Figure 8 - Graphic of increases (SCI) ΔL*, Δa*, Δb*, ΔAEab*, ΔC*, Δh* after the humidity and temperature accelerated artificial aging test after processing colorimetric data.

CONCLUSIONS

The best results have been obtained with Paraloid B72® and Mowital B60HH® fillers in general rates. They have good working properties and they are stable during the SO_2 saturated atmosphere accelerated artificial aging test, and also do not show any relevant changes compared to other fillers tested. Moreover, they possess high reversibility and resistance, which makes them ideal to apply to medium to small fossils. They also do not add high levels of humidity related to other fillers tested, and humidity is also under control.

Mowital B60HH® shows decohesion, revealed by its mass loss, cracking and porosity in samples after the SO_2 saturated atmosphere accelerated artificial aging test. This decohesion can be fixed by adding a larger quantity of resin during the preparation. Application of Paraloid B72® filler can be improved by using different solvents during the preparation, such as ethanol (Lastras Pérez, 2007). These improvements will be developed in future studies.

Epoxy gap fillers should be used only with large and resistant specimens because they are irreversible, due to the high adhesive power and high resistance they possess. There are no significant changes in mass, however, it is important to highlight that Epo 150® filler does not show any mass change after the accelerated artificial aging tests. Therefore, it can be stated that this is the most stable filler regarding mass changes over time. Despite these properties, Epo 150® fillers do add more weight to large specimens, which makes the handling of specimens more difficult. Furthermore, epoxy resins are really unreliable regarding chromatic changes after accelerated artificial aging tests. Araldit SV427® is the most unstable filler regarding the SO_2 saturated atmosphere accelerated artificial aging test and the UV radiation accelerated artificial aging test, compared to other fillers. It is also important to note that epoxy fillers appear to generate salt efflorescence after SO_2 saturated atmosphere accelerated artificial aging test. Also, it has to be noted that Araldit SV427® is a commercial preparation that could be changed by the producer, so mixture components could change at any moment (Loew Craft and Solz, 1998).

PVAs fillers are stable regarding changes in mass. PVAs filler without glass microballs register a mass change of 0, while PVAs filler with glass microballs added register a change in mass of 0,07 and -0,07. This could be due to the fact that glass microballs destabilize the filler regarding mass change. However, glass microballs do stabilize the filler regarding SO_2, humidity and temperature. These fillers display large problems of working properties: they give specimens high humidity levels because of their long drying periods, and it is also difficult to polish and level them. In addition, they are chromatically instable after UV radiation, and the SO_2 saturated atmosphere and humidity and temperature accelerated artificial aging tests.

Using an interlayer is recommended (López Amador and Pellejero, 2007) to avoid direct contact between gap fillers and specimens. In this way the treatment will be more reversible and also, fossils will be protected from salt contamination. In addition, purification of the fossil matrix used in the samples is proposed for future analysis.

Despite generalized use of Paraloid B72® and epoxy resins as a base of fillers in fossil reintegration, there are no studies yet where compatibility of gap fillers with different fossils is valued. Moreover, no study noted that epoxy resins do not keep conservation principles because they are not reversible and have a huge grade of yellowing.

It is important to consider the toxicity of gap fillers. Future research looking for alternative solvents is proposed, which are less harmful for conservators and the environment (Larkin and Makridou, 1999).

In conclusion, research results show factual data that have to be valued by conservators in order to select the best materials to be used during conservation process.

REFERENCES CITED

Aberasturi Rodríguez, A., R. Ferrer Bielsa, and A. Cobos Periáñez. 2009. Preparación de un fémur de dinosaurio (Colorado, EE.UU). Kausis: Revista de La Escuela Taller de Restauración de Pintura Mural de Aragón II 6:71–78.

Andrew, K. 2009. Gap fills for geological specimens: or making gap fills with Paraloid. NatSCA News 16:41–45.

Baeza Chico, E., and S. Menéndez. 2005. Conservación y restauración de amnonites piritizados del Museo Geominero (IGME, Madrid). Investigación En Conservación Y Restauración: II Congreso Del Grupo Español Del IIC:[9, 10 Y 11 de Noviembre de 2005, Barcelona] 47.

Baeza Chico, E., S. Menéndez, and A. Rodrigo. 2009. La reintegración en materiales paleontológicos. Criterios utilizados. Justificación y propuestas de intervención en el Museo Geominero (IGME, Madrid). IV Congreso Del GEIIC, 25th, 26th and 27th November 2009, Cáceres 207–217.

Davidson, A. 2009. Temporary gap-filling to stabilize an exploded matrix for fossil preparation: the sand and Butvar B-76 technique. Journal of Vertebrate Paleontology 29 (suppl. 3):85A.

Fox, M. 2001. Searching for the filler of my dreams - an odyssey in gaps and glues. Journal of Vertebrate Paleontology 21 (suppl. 3):51A.

Gisbert Aguilar, J., and C. Marín Chaves. 2001. Contaminación atmosférica y deterioro de monumentos. I Jornadas de Caracterización Y Restauración de Materiales Pétreos En Arquitectura, Escultura Y Arqueología. Zaragoza 327–342.

González Santiago, E., M. Belinchón García, and C. Pérez García. 2008. Restauración de un ejemplar de fósil de *Rana* sp., anfibio del yacimiento paleontológico de Rubielos de Mora (Teruel, España). 17th International Meeting on Heritage Conservation. 2008, Castellón 505.

Haugrud, S. J., and B. P. Compton. 2008. Reversible filler: a fresh look at Butvar-76. Journal of Vertebrate Paleontology 28 (suppl. 3):89A.

Howie, F. M. P. 1979. Museum climatology and the conservation of palaeontological material. Special Papers in Palaeontology 22:103–127.

Koob, S. 1998. Obsolete fill materials found on ceramics. Journal of the American Institute for Conservation 37:49–67.

Larkin, N. R., and E. Makridou. 1999. Comparing gap-fillers used in conserving sub-fossil material. Geological Curator: GCG 7:81–90.

Lastras Pérez, M. 2007. Investigación y análisis de las masillas de relleno para la reintegración de lagunas cerámicas arqueológicas. Ph. D. dissertation, Universitat Politècnica de València, Valencia, Spain, 438 pp.

Lastras Perez, M., M. Martinez Bazan, and B. Carrascosa Moliner. 2007. Estucos en la reposicion de faltantes de azulejeria expuesta en el exterior. Estudio de los cambios colorimetricos tras distintos ensayos de envejecimiento acelerado. Arche: Publicacion Del Instituto Universitario de Restauraction Del Patrimonio de La UPV 2:95–98.

Leiggi, P., and P. May. 2005. Vertebrate Paleontological Techniques. Cambridge University Press, Cambridge, UK, 372 pp.

Loew Craft, M., and J. A. Solz. 1998. Commercial vinyl and acrylic fill materials. Journal of the American Institute for Conservation 37:23–34.

López Amador, J., and I. Pellejero. 2007. Técnicas de preparación de fósiles en yacimientos paleontológicos. Consolidación "in-situ" para exponer temporalmente en Orce, Granada. Laboratorios de paleontología. ¡Fundamental! 10:31–40.

Martínez Bazán, M. L. 2007. Colorimetría Aplicada Al Campo de La Conservación Y Restauración: Curso: Máster/Doctorado. Universidad Politécnica de Valencia, Valencia, Spain.

Martínez Riera, T. M. 2015. Estudio del comportamiento físico-mecánico en masillas de relleno y sellado para la reintegración formal en material fósil. Master Thesis, Universitat Politècnica de València, Valencia, Spain, 192 pp.

Mas Barberà, X. 2008. Estudio y caracterización de morteros compuestos, para su aplicación en intervenciones de sellados, reposiciones y réplicas, de elementos pétreos escultórico-ornamentales. Ph. D. dissertation, Universitat Politècnica de València, Valencia, Spain, 413 pp.

Romero, G., M. Mancheño, and J. Carlos. 2007. Hallazgo de una tortuga gigante fósil en el Puerto de la Cadena (Murcia). XVIII Jornadas de Patrimonio Cultural. Intervenciones En El Patrimonio Arquitectónico, Arqueológico Y Etnográfico de La Región de Murcia, Murcia, Spain 13–25.

Thornton, J. 1998. A brief history and review of the early practice and materials of gap-filling in the West. Journal of the American Institute for Conservation 37:3–22.

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CONSOLIDATION OF BONE MATERIAL: CHROMATIC EVOLUTION OF RESINS AFTER UV ACCELERATED AGING

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ABSTRACT

Choice of conservation treatments for archeological bone material is a complex issue. Consolidation in affected zones by decohesion with Acril-33 and Paraloid™ B-72 is one of the most common interventions for stabilization. These materials are extremely sensitive to UV radiation, which render them whitish and brittle. This study assesses the stability level in several acrylic and vinyl resins applied as consolidant or adhesive in archeological materials. Therefore, we prepared concentrations in different solvents at 5% with a UV stabilizer Tinuvin® 292. Colorimetry shots were made with a spectrophotometer before and after consolidating bone fragments and during an aging process of 240 hours of exposure to UV radiation, in order to understand if long term changes could be perceived.
Results are variable because of the particular characteristics that every bone fragment has. We thus confirm differences in behavior and final appearance of the original material, depending on the combination of resins and consolidants used during conservation and restauration. Therefore, additional studies and tests of solvent combination will be necessary to assess their effects in more detail.

Keywords: aging; bone; consolidation; colorimetry

RESUMO [in Portuguese]

A escolha do tratamento adequado para a conservação de material ósseo arqueológico é um assunto complexo. As zonas descoladas são comumente consolidadas usando Acril-33 e Paraloid™ B-72 para as estabilizar. Estes materiais são extremamente sensíveis à radiação UV o que os pode tornar quebradiços e esbranquiçados. Este estudo avalia o grau de estabilidade de várias resinas acrílicas e vinílicas como consolidantes ou adesivos em materiais arqueológicos. Assim, preparámos concentrações de 5% em diferentes solventes com o estabilizador UV Tinuvin® 292. Foram feitos testes de colorimetria com um espectrofotómetro antes e depois dos fragmentos ósseos terem sido consolidados, bem como, durante um período de 240 horas de exposição à radiação UV, de forma a compreender se seria possível detectar quaisquer alterações de longo termo.
Os resultados foram variáveis devido às características particulares que cada fragmento de osso apresenta. Desta forma confirmamos diferenças no comportamento e aparência final do material original, dependendo da combinação de resinas e consolidantes usados durante a conservação e restauro. Por esse motivo, serão necessários mais estudos e testes às combinações de solventes para aferir os seus efeitos em maior detalhe.

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INTRODUCTION

Osteological materials are very sensitive when the remains are excavated; they are anisotropic and hygroscopic materials, with the ability to retain or transfer water to the atmosphere. When the remains are adapted to the environment's relative humidity, they can suffer directional deformation in each of their three axes. This new condition causes problems of contraction and expansion. The volume changes and the tensions triggered by these new conditions result in fractures, cracks, fissures, and streaking following the axes of the bone tissue, increasing the instability of the piece. The fractures start when the imposed stress exceeds the strength limits of the material (Laborde Marqueze and Bouzas Abad, 2003).

Sunlight sensitivity is another very important factor in the preservation of archeological bone; a long exposure promotes an increase of brittleness and the loss of their natural color (Plenderleith, 1967). Because of this, the best way to conserve and preserve the bone is to establish steady relative humidity (RH) and temperature values the 45-55% RH and 25°C (Stone et al., 1990), and to adapt the bone gradually to these conditions from their unearthing until their conservation intervention in a humidity box at the laboratory. Thereby, exposure to rapid fluctuations that might cause possible damage resulting from mechanical stresses can be prevented.

The alteration processes depend on the chemical composition of the archeological material, its physical characteristics, and the soil environment, including acidity and alkalinity, presence of soluble and insoluble salts, degree of aeration, water movement and climatic changes where they have been deposited (Koob, 1984; Johnson, 1994). As a consequence, deterioration of specimens or bone remains varies in velocity and severity, and in the same specimen we can find different states of preservation as a result of the diversity of the chemical components. The qualities such as porosity, density, hardness, size and bone shape transform these organic materials in a very complex and heterogeneous unit. In sum, its state of preservation depends more on the soil and climate than its chronological age (Brothwell, 1993).

The archeological remains go through various treatments of conservation, from its excavation until its musealization. The preventive measure of stabilization includes monitoring the levels of HR, temperature and lighting (Porto Tenreiro, 2000). The conservation interventions have to be adapted to the purpose or the scientific interest, the most common of them being cleaning, consolidation and assembly of fragments. The Decalogue of the Conservation recommends minimal intervention judgement. The limitation of the interventions to a minimum is due to the respect for the original material and to keep its integrity for future research. It is very important to find a balance in the intervention standards because the quality of the information might be affected in further research also at microscopic scale, as for instance chemical analyses, which might yield misleading results as a consequence of the cleaning and consolidation treatment (Johnson, 1994; López-Polin et al., 2008a).

Materials used for consolidation

The methodology for the consolidation of osteological specimens has been inadequate in many cases, because of incomplete knowledge of the materials and methods applied. Commonly used consolidants or "preservatives" during historical conservation interventions were paraffin wax, beeswax or mixtures of resin wax (Koob, 1984). These materials are difficult to remove and cause metric inaccuracies due to the thickness of the layer applied to the bone surface (Brothwell, 1993). Shellac was commonly used in dense layers, affecting coloration and producing surface gloss (Figure 1). Moreover, these layers become unstable over time and form a hard layer that cracks and begins to peel and fall off of the surface of the bone (Brothwell, 1993; Johnson, 1994; Pasíes Oviedo, 2014). Other natural consolidants have also been used, such as glue solutions or isinglass and animal glue (Rathgen, 1905; Johnson, 1994). An example of a common consolidant is cellulose nitrate resin (Johnson, 1994; Pasíes Oviedo, 2014), although its instability was recognized since 1936 (Johnson, 1994). The cellulose nitrate resin develops severe yellowing, and becomes brittle and flakes away, but it is still used because it can be easily obtained (Johnson, 1994).

In addition to the natural and cellulose nitrate resins, the most common synthetic resins used in consolidation of bone materials have been: poly(vinyl) acetal resins, poly(vinyl) butyral resin, poly(vinyl) acetal resins, poly(vinyl)

Figure 1 - Example of consolidation of bone material with Shellac. Left: left lateral view; Right: ventral view. Note the surface gloss and differences in color. Image: Archivo del Museu de Prehistòria de València, used with permission.

acetate emulsions, acrylic emulsions, acrylic colloidal dispersions and acrylic resins (Johnson, 1994). The references published recommend the use of polyvinyl acetate and acrylic resins such as Paraloid™ B-72 (Acryloid B-72 in the US) in concentrations of 5 to 10% solution in acetone or toluene, as well as the use of emulsions of polyvinyl acetate (PVA) and acrylic for consolidation of damp bones.

Nowadays, at least in Spain, the use of vinyl resins in the consolidation of archeological bone materials is no longer common. It has been predisposed by acrylic resins (Paraloid™ B-72) in acetone solution and acrylic emulsion (Primal AC-33, Acril 33) in concentrations between 3 to 10% (García Fortes and Flos Travieso, 2008; López-Polin et al., 2008b) or 4-5% (Canci and Minozzi, 2005). Due to its difficult reversibility, emulsions like Primal AC-2404 are no longer used in restoration of paleontological material (López-Polin et al., 2008b). After a natural aging, acrylic resins become insoluble in low polarity solvents (Borgioli and Cremonesi, 2005).

The choice of the most appropriate kind of consolidant depends on whether the material is wet or dry and the judgment of the restorer. It can be applied by spraying, dripping, brush impregnation, injection, immersion and impregnation under vacuum or pressure.

Inadequate interventions not only result from the choice of the consolidant, but also of its application. Nowadays, invasive treatments such as immersion and pressure impregnation are discarded. These application methods change the hue and brightness of the bone surface (Pasíes Oviedo, 2014), generate problems in the transpiration of the material, and induce physical-chemical changes in the composition and internal structure of the original components. Furthermore, the treatments may influence the results of the analysis of obtaining absolute dates (López-Polín et al., 2008a) and hamper a correct observation of the surface through electron microscopy (SEM) (Fernández-Jalvo and Marín Monfort, 2008). In addition, it is difficult to remove the consolidant without damaging the bone morphology (Johnson, 1994). Current judgment and professional experience suggest its application only when it is strictly necessary.

Long term behavior of synthetic resins from the industry is often unknown. The fact that we consider these materials appropriate today, does not mean that the stability and aesthetic vision will not be affected over short or long periods of time.

The combined action of light and changes in temperature and relative humidity affect the stability of the specimen and the products used in the intervention, but the specimen and the conservation materials can age differently.

Here, we assess the consolidating stability after exposure to ultraviolet radiation, which simulates aging. Ultraviolet radiation is a punctual treatment that can alter the original appearance. Changes in brightness and yellowing over time can be detected visually, with or without a microscope.

Solvents

Different solvents can strongly vary in their penetration ability. The factors that we must consider in the selection of the solvent and the consolidation process are (García Fortes, 2001):

- Nonpolar solvents with a low surface tension have the highest capacity of penetration. Water is a polar solvent with very low penetration capacity.
- Consolidants in a solution have better penetration capacities than emulsions.
- Less volatile solvents can increase their ability of penetration in the porous structure because they remain more time on the surface of the object to be consolidated.

Polarity and toxicity of the solvent should be considered during the selection of the most appropriate solvent. Highly toxic solvents such as aromatic hydrocarbons (e.g. toluene and xylene) have not been in use now for some time. Toluene was used individually or combined with acetone as consolidant for the conservation of bone and paleontological material, because it increases the drying time and thus facilitates penetration (Koob, 1984). Acetone, an organic solvent, is the most common diluent for Paraloid™ B-72, but its high volatility generates a reverse migration effect. Because of this high volatility and the resulting reverse migration, Borgioli (2007) recommended the use of Butyl acetate and Dowanol PM instead of acetone and ethyl acetate for the solubilization of Paraloid™ B-72.

Consolidants

The objectives of consolidation are to restore its original density and return to the material's structural capacity, which has been lost as a consequence of prolonged negative impact of the physical, chemical and biological agents over time. The consolidants are only applied if strictly necessary. They should not be indiscriminately applied, because they modify the properties of the original material and can obstruct the constant fluctuations. Even if previously applied resins can be removed, the conservation treatment might have altered the original material, which precludes important future studies (optical and electronic microscopy) and chemical results (López-Polin et al., 2008a).

It is very difficult to find a material that meets most of the characteristics of a good consolidant (Koob, 1984; Johnson, 1994). The requirements to select the most appropriate material are:

- To offer strong cohesion that allows future manual manipulation of the material.
- Regarding the original material it must be compatible and stable.
- They must not cause disturbances in either the structure or in the appearance during application as after natural aging (Horie, 1987).
- Suitable impregnations properties, appropriate flexibility and hardness, easy application, long term reversibility (Horie, 1987; Kres and Lovell, 1995)
- Reversibility approach: The reversibility and total elimination of the resin is relative, because their total elimination from the pores of the material is impossible. Also, if the objective is the restoration of the structural capacity of the original material, the removal of the consolidant would endanger the physical integrity of the specimen (García Fortes and Flos Travieso, 2008). The reversibility approach is thus more focused on color variation and brightness caused by excessive use of consolidants.

The viscosity, particle size, solvent system, glass transition temperature (Tg), pH and toxicity are other characteristics that we have to consider in the selection of the consolidating resin (Koob, 1984).

METHODS

Samples were exposed to UV radiation, which artificially accelerates aging, in order to test the stability of the resins used during the conservation intervention and if their application was made in an appropriate way. This methodology was selected because UV radiation is one of the major causes of diminution of stability of the resins and the surface changes. The objectives were to 1) confirm if the added materials present compatibility, affinity and symmetrical aging, and 2) prove if the addition of the stabilizer Tinuvin® 292 UV incorporated into the consolidant would reduce the whitening of the bone material. In order to test this, our study protocol was the following:

- Selection of resins and preparation of consolidants.
- Measure the distance of capillarity in paper strip (following Fedak, 2006).
- Preparation of stencil for further controls of chromatic variations on bone surface and glass slides (for neutral surfaces).

- Application of the consolidants on the glass slides.
  - Observation the effects of the consolidant: white veil, distribution and drying.
- Selection and preparation of the bone remains.
- Photography with optical microscopy (before consolidation).
- Impregnation brush on the archaeological bone material.
- Photography whit optical microscopy (after consolidation).
  - Observation of the morphological changes: distribution and drying the consolidant and if this form white veil or brightness.
- Accelerated aging by exposure to UV light in Q-BASIC UV with a UVA-340 nm lamp.
- Chromatic analysis by visible Spectrometry / Colorimetry: The color measurements were performed with a Spectrophotometer Minolta CM-2600d, which determines the CIE tristimulus values (X, Y, Z) with Ø 5mm measurement area. Measurements were made with the standard illuminant CIE type D65 (day light, color temperature 6500ºK) and the standard observer 10º (KONICA MINOLTA SENSING, Inc.) with specular included (SCI) and excluded (SCE).

For the evaluation of the changes in color, the CIELAB and CIELCH perceptives were used. The total chromatic difference between two stimuli is calculated using the CIEDE 2000 (ΔE_{00}) equation, which is the most recent recommendation of the CIE (Melgosa et al., 2001):

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)}$$

The glass slide was subjected to Stove Aging in order to assess yellowing. For the calculation of the degree of yellowing, we used the tristimulus values XYZ provided by the spectrometer. The yellowness index (IY) (ASTM D1025; González & Leal, 2008) is calculated with the following equation:

$$YI = \left(\frac{X - Z}{Y}\right) X\,100$$

For each of these two assessments of color change, three samples were prepared. As recommended in the European normative test methods for color measurement of surfaces, UNE-EN 15886, established for the conservation of cultural property, we carried out five measurements.

The colorimetric monitoring was realized at 0, 24, 72, 120 and 240 h exposure of UV radiation.

- Photography with optical microscopy after 240h exposure of UV radiation.
  - Study of morphological changes: Observation of possible changes in brightness and whitening of the surface.

We applied the colorimetry to assess chromatic variations after conservation processes or mere aging. If we expose samples to accelerated artificial aging, we will obtain data concerning their resistance over time. The results provide information on the best choice of consolidants and restauration treatments of all kind of bone and other archeological materials.

Consolidant selection

To carry out this study we selected some resins used as consolidants (preservatives) and adhesives in the area of conservation of cultural heritage. The concentrations were produced in proportion weight to volume (w/v) in different solvents are shown in Table 1.

Acril-33 (acrylic EA / MMA) was selected as an example of acrylic emulsion resins, because of its characteristics and resistance to aging. Acril-33 is employed in many sectors of the conservation cultural heritage.

We selected different solvent based acrylic resins. On the one hand, we selected Evalcite® 2044 (acrylic nBMA) for its elasticity. Its application is recommended for materials subject to dimensional changes (wood, leather, parchment, etc.). On the other hand, we selected a wide range of Paraloid´s series: Paraloid™ B-66 (acrylic MMA/BMA) for its optimal characteristics of adhesion and flexibility, although its yellowness changes with temperature; Paraloid™ B-72 (acrylic MA/EMA) because it is considered the most stable methacrylate, and for other characteristics such as reversibility, resistance to oxidation, to light, to hydrolysis, to moderate heat and mechanical strength; Paraloid™ B-82 (acrylic MMA) has the special property of being soluble in alcohol/water mixtures and has 9,4 solubility; and finally, a mixture of Paraloid™ B-72 and 44 to add the elasticity and increase glass transition temperature (Tg) of the Paraloid™ B-72.

Table 1 - Consolidants tested with UV accelerated aging.

RESINS		tg	SOLVENT	OTHERS (UV Stabilizer)	%	ACRONYM
ACRYLIC	Acril®-33		WATER	-	5%	AC-
	EVALCITE 2044	15 ºC	ACETONE	-	5%	EV-A-
			ACETONE	TINUVIN 292	5%	EV-A+T-
			ETHYL ACETATE	-	5%	EV-EA-
			ETHYL ACETATE	TINUVIN 292	5%	EV-EA+T
			ACETATE OF BUTILO	-	5%	EV-B
			ACETATE OF BUTILO	TINUVIN 292	5%	EV-B+T-
			DOWANOL PM	-	5%	EV-DW-
			DOWANOL PM	TINUVIN 292	5%	EV-DW+T
	PARALOID B-44	60 ºC	ACETONE	-	5%	P44-A
			ACETONE	TINUVIN 292	5%	P44-A+T
			ACETONE:ETHYL ALCOHOL	-	1:1 5%	P44-1:1
			ACETONE:ETHYL ALCOHOL	TINUVIN 292	1:1 5%	P44-1:1+T
			ETHYL ACETATE	-	5%	P44-EA
			ETHYL ACETATE	TINUVIN 292	5%	P44-EA+T
			ACETATE OF BUTILO	-	5%	P44-B
			ACETATE OF BUTILO	TINUVIN 292	5%	P44-B+T
			DOWANOL PM	-	5%	P44-DW
			DOWANOL PM	TINUVIN 292	5%	P44-DW+T
	PARALOID B-66	50 ºC	ACETONE	-	5%	B66-A
			ACETONE	TINUVIN 292	5%	B66-A+T
			ACETONE:ETHYL ALCOHOL	-	1:1 5%	B66-1:1
			ACETONE:ETHYL ALCOHOL	TINUVIN 292	1:1 5%	B66-1:1+T
			ETHYL ACETATE	-	5%	B66-EA
			ETHYL ACETATE	TINUVIN 292	5%	B66-EA+T
			ACETATE OF BUTILO	-	5%	B66-B
			ACETATE OF BUTILO	TINUVIN 292	5%	B66-B+T
	PARALOID B-72	40 ºC	ACETONE	-	5%	B72-A
			ACETONE	TINUVIN 292	5%	B72-A+T
			ACETONE:ETHYL ALCOHOL	-	1:1 5%	B72-1:1
			ACETONE:ETHYL ALCOHOL	TINUVIN 292	1:1 5%	B72-1:1+T
			ETHYL ACETATE	-	5%	B72-EA
			ETHYL ACETATE	TINUVIN 292	5%	B72-EA+T
			ACETATE OF BUTILO	-	5%	B72-B
			ACETATE OF BUTILO	TINUVIN 292	5%	B72-B+T
			DOWANOL PM	-	5%	B72-DW
			DOWANOL PM	TINUVIN 292	5%	B72-DW+T

RESINS		tg	SOLVENT	OTHERS (UV Stabilizer)	%	ACRONYM
ACRYLIC	PARALOID B-82	35 ºC	ACETONE	-	5%	B82-A
			ACETONE	TINUVIN 292	5%	B82-A+T
			ACETONE:ETHYL ALCOHOL	-	1:1 5%	B82-1:1
			ACETONE:ETHYL ALCOHOL	TINUVIN 292	1:1 5%	B82-1:1+T
			WATER: ETHYL ALCOHOL	-	1:9 5%	B82-1:9
			WATER: ETHYL ALCOHOL	TINUVIN 292	1:9 5%	B82-1:9+T
			ETHYL ACETATE	-	5%	B82-EA
			ETHYL ACETATE	TINUVIN 292	5%	B82-EA+T
			ACETATE OF BUTILO	-	5%	B82-B
			ACETATE OF BUTILO	TINUVIN 292	5%	B82-B+T
			DOWANOL PM	-	5%	B82-DW
			DOWANOL PM	TINUVIN 292	5%	B82-DW+T
	PARALOID B-72+44 (1:1)		ACETONE	-	5%	P50-A
			ACETONE	TINUVIN 292	5%	P50-A+T
			ACETONE:ETHYL ALCOHOL	-	1:1 5%	P50-A:A
			ACETONE:ETHYL ALCOHOL	TINUVIN 292	1:1 5%	P50-A:A+T
			ETHYL ACETATE	-	5%	P50-AE
			ETHYL ACETATE	TINUVIN 292	5%	P50-AE+T
			ACETATE OF BUTILO	-	5%	P50-B
			ACETATE OF BUTILO	TINUVIN 292	5%	P50-B+T
			DOWANOL PM	-	5%	P50-DW
			DOWANOL PM	TINUVIN 292	5%	P50-DW+T
VINYL	VINNAPAS LEF 10W		WATER		5%	VN
	MOWITAL B60HH		ETHYL ALCOHOL	-	3%	MW
			ETHYL ALCOHOL	TINNUVIN	3%	MW+T
	K 60		ETHYL ALCOHOL	-	3%	K-E
			ETHYL ALCOHOL	TINUVIN 292	3%	K-E+T
			ACETONE	-	3%	K-A
			ACETONE	TINUVIN 292	3%	K-A+T
			ACETONE:ETHYL ALCOHOL	-	1:1 3%	K-A:A
			ACETONE:ETHYL ALCOHOL	TINUVIN 292	1:1 3%	K-A:A+T
			ACETATE OF BUTILO	-	3%	K-B
			ACETATE OF BUTILO	TINUVIN 292	3%	K-B+T
			DOWANOL PM	-	3%	K-DW
			DOWANOL PM	TINUVIN 292	3%	K-DW+T
FLUORIDE ELASTOMERS	FLUOLINE A		ACETONE	-	15%	FA-

VINNAPAS® CEF 10W (used as consolidant for the adhesive formulations, varnishes and paints) was studied for comparisons with emulsion acrylic resins.

Among the solvent based vinyl resins, we selected the K60 (PVA) and Mowital® B60HH (polininilbutirrale) for their resistance to aging and their reversibility characteristics in alcohol. Their main use is for gluing and the consolidation of archeological ceramics.

Finally, FLUOLINE A, a kind of fluoride elastomers and acrylic polymers in acetone, was selected due to its recommendation for gluing and pre-consolidation of wood, stone, clay, fossils, archeological remains, and more. Tinuvin® 292 UV filter was added to the solvent resins because it is recommended to reduce effects of UV radiation in varnishes based on synthetic and natural resins.

Preparation of samples for testing

We have selected bone fragments out of context of the Archaeological Museum of Lliria (Valencia, Spain) in order to perform studies on original material. The consolidation was made by impregnation brush in all fragments (Figure 2).

RESULTS

Consolidants on glass slides

Visual observation

We made the following observations during the impregnation of the consolidants with a brush on the glass slides:

- The brushstrokes are visible with all resins dissolved in acetone while the solvent is evaporating.

Figure 2 - Bone fragments selected for test and consolidating process.

- K60 and Mowital® B60HH vinyl resins dissolved in ethyl alcohol evaporate slower, allowing for a uniform application, and form a homogeneous film.
- The Paraloid solutions in mixtures of 1:1 ethyl alcohol/acetone and Paraloid™ B-82 in 1:9 water/ethyl alcohol mixtures have increased drying times and form homogeneous films, but also white veils.
- The behavior of resins dissolved in ethyl-acetate is similar to the one of solutions in acetone. However, brushstrokes are less visible.
- In the following condition: acetone, ethyl-acetate, butyl acetate, and Dowanol PM, the drying time is increasing and the distribution for the surface is more uniform due to the low volatility of the solvent.
- Emulsion resins have the longest drying time.

Similar results were obtained by the absorption capillarity test in 60 seconds on strips of paper:

- A higher concentration of the resin results in a lower capacity of penetration by capillary forces.
- The results of the two emulsion resins (Acril-33 and Vinnapas® Lef 10w) are similar; both take much time in drying and in starting to form a hard film.
- Even though the vinyl resins are dissolved in ethyl alcohol (which has a low volatility, and should thus penetrate more easily), their penetration index depends on the concentration of the solution. In low concentrations, vinyl resins have a lower penetration index than acrylic resins.
- Apparently, the acrylic resins dissolved in acetone have a higher capacity of penetration, but this is not the case, because the rapid evaporation of acetone does not permit the resins to enter the internal structure. In this case, 60 seconds after application of the resin on the strips of paper, there is a humid area but the hard film does not remain in the entire area after the solvent has evaporated.
- Fluoline A resin has an absorption capacity by capillarity similar to acrylic resins.

Chromatic changes after test in oven

Yellowness Index is used to measure the types of deterioration. These types of deterioration are associated with oxidation, surface dirt and other relevant developments that lead to the degradation of the resin, which is subject to radiation and atmosphere (González and Leal, 2008). To estimate the Yellowness Index increment in the resins, the samples were introduced for 72 h in the oven with a potassium sulphat dissolution (UNE 48-071-82). As shown in the Tables AI-1 and AI-2, the results when adding Tinuvin® 292 are more or less similar to what we obtained without it application. Therefore, Tinuvin® 292 does not fulfill its essential function of UV filtering in this context.

The results of this test were the following (see also Table AI-1):

- The vinylic resins tested tend to turn yellow. The consolidants produced with Mowital® are affected most. The most stable is K60 dissolved in ethyl alcohol.
- An increased yellowing rate can be observed in more acrylic resins as Acril-33, Evalcite® and many paraloids.

- Paraloid™ B-72 is the resin most used as consolidant in the conservation of archeologic materials. When the resin is dissolved in acetone or an acetone:ethyl alcohol mixture, it is strongly affected by yellowing. In these cases we have observed the filter effectivity of Tinuvin® 292. The best results were obtained with solutions in acetate ethyl, acetate butyl and Dowanol.

Chromatic changes after accelerated aging with UV (see Table AI-2)

- Vinylic resins: there are no perceptible changes in color, with ΔE00 lower to 1,00 unit CIEDE00. The generated darkening coincides entirely with the Yellowing Index. The worst results are produced with Mowital®. We can confirm that the effects of Tinuvin® 292 make the resin less stable.
- Acrylic resins: the tested acrylic resins have similar, stable behaviors with less than one unit in the ΔE00 after UV aging, except Paraloid™ B-72 in acetone and Paraloid™ B-82 in a acetone/ethyl alcohol mixture. When the Paraloid™ B-72 is solved in Dowanol PM and ethyl acetate, good results were obtained with 0,12 units approximately compared to acetone with 0,67 units CIEDE00 of the total color difference. Some darkening can be observed in Evalcite® samples according to the lightness value L*.
- Fluoline-A samples give good results (0,14 units ΔE00).

Consolidation of bone material

Chromatic changes of the consolidated bone material after accelerated aging with UV

The consolidated bone specimens were exposed to 240 h of UV accelerated aging. The measurements of two or three samples of each preparation of resins is shown in Table AIII-1 (where all detailed information from all tests

Figure 3 - Bone remains and highlighted points for colorimetric measure.

can be consulted). Average values were calculated from five measures, as recommended by the normative UNE-EN 15886. The monitoring was realized in the points highlighted in Figure 3.

The behavior of the resins was evaluated through comparisons with untreated areas.

CIELCH Diagrams (Figures AII-1 to AII-11) indicate that the total color changes (ΔE00) exceeded the visible threshold (Melgosa et al., 2001). All of them reached values above the 1,75 unites CIEDE00 after exposure of 24-72 h to UV radiation. The changes augmented with increasing exposure time, because the photodegradation is accumulative.

The color changes in untreated areas are very variable; there are changes between 1,55 to 18,61 units. This disparity could be because the stability of each fragment or tested area depends on its composition, porosity, deterioration, and other factors. Therefore, we established a maximum limit to color change acceptability at 2 units CIEDE00.

Most changes were observed in areas consolidated with Acril-33 and Vinnavil. The samples treated with K60 showed no changes between consolidated and untreated areas. Color was only more stable when applying K60 dissolved in acetate butyl. Fluoline-A provided good results, given that the first changes start after 120h of exposure to UV radiation.

Differences were observed depending on the solvent employed in all Paraloid:

- Paraloid™ B72+44: The best behaviors are presented at the areas consolidated with the resin dissolved in acetate butyl in all increments or CIE Colour Space Notations (ΔL*, ΔE00*, ΔC* and Δhº). In addition, the areas treated with resin dissolved in DOWANOL PM yield optimal results. There are no specific observable changes after UV test in treated and untreated surface areas.

The worst results are produced when dissolved in acetone and/or ethyl acetate.

Paraloid™ B-44, B-66 and B-82: there were more changes in the treated areas than in the untreated areas. When consolidated with B-44, independently from the solvent used, it became more opaque as a result of less chroma (ΔC*).

- Paraloid™ B-72: as shown in Figure AII-9 the consolidated areas of the same bone treated with resin dissolved in ethyl acetate and butyl acetate is different. Compared to the untreated area, the total color change, the lightness level and the loss of chromaticity is more stable after application of solutions in butyl acetate.

All coordinates are located within the yellow-red (+b, +a) range on the CIELAB diagram. The untreated bone material undergoes a slight yellowing and becomes less chromatic (more matt) and lighter in respect to L*. These results are similar to the bone treated with any resin except for the areas consolidated with Paraloid™ B-66 and B-82, where displacement of the coordinates is more extensive.

DISCUSSION

The group of consolidants applied to the glass slide were classified as belonging to category I Lightfastness I, according to the standard ASTM 4303-03, given the obtained changes of less than four units in the total color change (ΔE_{00}) after exposure of 240 h to UV radiation. These results are different in the original material depending on its characteristics.

As shown in Figures 4 and 5, where it has been done a visual appreciation of the morphological changes using the optical microscopy after UV accelerated aging, the same fragment can have areas of varying sensitivity to UV radiation, given the variable color changes across the object.

Figure 4 - Bone fragments before (a) and after (b) UV radiation test.

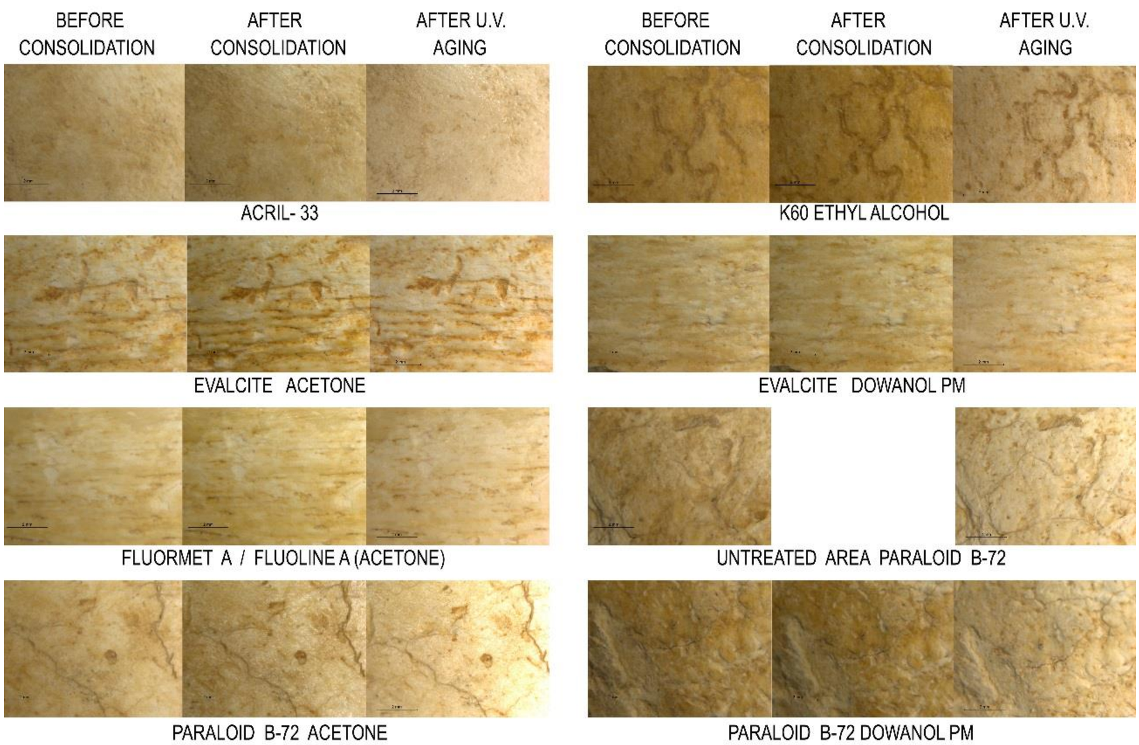

Figure 5 - Selection of consolidated areas indicating color changes before and after consolidation, and after exposure to UV.

Summary and recommendations

The UV filter Tinuvin® 292 does not protect archeological bone material from UV accelerated aging. Therefore, we do not recommend its use in the preparation of resins for consolidation.

The solvent strongly affects the behavior of the resin when exposed to UV radiation. Most importantly, the degree of yellowing depends on the solvent used in the preparation of the resins.

All resins tested on glass slides were stable during exposure to UV radiation, yielding positive results concerning color changes with values below one unit CIEDE00. However, depending on the nature of the material treated and the state of degradation of the bone fragment, the result is different. Therefore, the stability of the consolidant depends on: the resin, the solvent and the bone´s characteristics (composition porosity, state of degradation, and other factors).

The vinyl resin Vinnapas®, applied in a 5% solution (v/v), yielded similar results as acryl resin Acril-33. When choosing emulsion resins, one should bear in mind that over time, these resins tend to change chemically to form more extensive cross-linking. The resins will become insoluble as a result of the presence of additives, emulsifying agents, and stabilizers necessary for keeping the resin in suspension (Sease, 1994).

Changes in color were most apparent when applying Mowital® and K60, as indicated by the Yellowness Index. The vinyl resin K60, when dissolved in acetone, ethyl-acetate, acetate butyl, and Dowanol PM, produces surface gloss and is less stable than some acrylic resins. Generally, vinyl resins show worse results than the acrylic resins and are not recommended because of their sensitivity to changes in temperature (Sease, 1994).

There are more changes in consolidated areas with Acril-33, Paraloid™ B44, B-66 and B-82, as surface gloss, yellowing, or the appearance of white veils, compared to the other tested resins. The use of these resins for the preparation and conservation of subfossil and fossil material is therefore not recommended.

After the E.A.A U.V test, the Evalcite® resin did not satisfy the expectations given the high levels of yellowness. This resin is less stable than the Paraloid group concerning the effects of UV light. Paraloid™ B-72 and Paraloid™ B-72+44 5% w/v yield better results dissolved in butyl acetate or Dowanol PM than acetone or ethyl-acetate. The use of other solvents than acetone or ethyl-acetate for Paraloid resins not only improved the stability of these resins, but also prevented inverse migration. Inverse migration counters penetration of the resin into the bones, because the high volatility of acetone or ethyl-acetate pulls the still dissolved resins back towards the surface.

Application of Fluoline-A resin as a consolidant has yielded good results. No yellowing of the resin, changes in brightness, nor visible differences in the consolidated areas were recognized. Testing should thus be continued with the many other existing types of Fluoline resins, in order to better understand their suitability as consolidators.

FUTURE DIRECTIONS

This study allowed us to assess chromatic changes produced in consolidated areas of archeological bone material after prolonged exposure to UV radiation.

Given that each solvent has advantages and disadvantages, no single solution exists for all preparation and conservation treatments. Further studies are needed to test additional solvent combinations. For instance, acetone can be partly substituted by Dowanol PM. Such a combination should provide increased penetration rates in internal, porous bone structures as a consequence of the lower density of Dowanol PM, and would also reduce the toxicity.

For the choice of resins and solvents, humidity and temperature have to be taken into account as well. Future analytical tests therefore need to include tests of humidity and temperature to assess the behavior of the resins under exposure to environmental fluctuations.

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REFERENCES CITED

Borgioli, L. 2007. Disolventes de Baja Toxicidad. CTS España. Productos y equipos para la restauración, Madrid, Spain, 7 pp.

Borgioli, L., and P. Cremonesi. 2005. Le Resine Sintetiche Usate Nel Trattamento Di Opere Polichrome. Il Prato, Saonara, Italy, 189 pp.

Brothwell, D. R. 1993. Notas orientativas para la excavación y la redacción de informes sobre restos humanos; pp. 11–40 in Desenterrando huesos. La excavación, tratamiento y estudio de restos del esqueleto humano. S.L. Fondo de Cultura Economica de España, Madrid, Spain.

Canci, A., and S. Minozzi. 2005. Archeologia Dei Resti Umani: Dallo Scavo Al Laboratorio. Carocci, Rome, Italy, 258 pp.

Fedak, T. J. 2006. Using capillarity for determining and maintaining a polymer consolidant concentration after solution preparation. Collection Forum 20:108–112.

Fernández-Jalvo, Y., and M. Marín Monfort. 2008. Experimental taphonomy in museums: Preparation protocols for skeletons and fossil vertebrates under the scanning electron microscopy. Geobios 41:157–181.

García Fortes, S. 2001. La terracota como elemento ornamental en la arquitectura de Barcelona. Técnicas de fabricación, Conservación y Restauración. Ph. D. dissertation, Universitat de Barcelona, Barcelona, Spain, 294 pp.

García Fortes, S., and N. Flos Travieso. 2008. Conservación Y Restauración de Bienes Arqueológicos. Editorial Síntesis, Madrid, Spain, 218 pp.

González, E., and J. Leal. 2008. Comportamiento de consolidantes de metales sometidos a envejecimiento acelerado. Bienes Culturales: Revista Del Patrimonio Histórico Español 8:223–231.

Horie, C. V. 1987. Materials for Conservation: Organic Consolidants, Adhesives, and Coatings. Butterworths, London, UK, 281 pp.

Johnson, J. S. 1994. Consolidation of archaeological bone: a conservation perspective. Journal of Field Archaeology 21:221–233.

Koob, S. P. 1984. The consolidation of archaeological bone. Studies in Conservation 29:98–102.

Kres, L. A., and N. C. Lovell. 1995. A comparison of consolidants for archaeological bone. Journal of Field Archaeology 22:508–515.

Laborde Marqueze, A., and A. Bouzas Abad. 2003. La degradación del hueso. Monte Buciero 267–275.

López-Polín, L., A. Ollé, I. Cáceres, E. Carbonell, and J. M. Bermúdez de Castro. 2008a. Pleistocene human remains and conservation treatments: the case of a mandible from Atapuerca (Spain). Journal of Human Evolution 54:539–545.

López-Polín, L., G. Gómez Merino, M. D. García-Antón Trassierra, N. I. López, A. Solé, J. G. Forès, A. Martín, J. Vilalta, P. Fernández, E. Lacasa Marquina, A. Bertral, B. Font, M. E. Nadal, and E. Carbonell i Roura. 2008b. La restauración de restos óseos e industria lítica en los yacimientos pleistocenos de la Trinchera del Ferrocarril (Sierra de Atapuerca, Burgos). Pátina 33–44.

Melgosa, M., M. M. Pérez, A. Yebra, R. Huertas, and E. Hita. 2001. Algunas reflexiones y recientes recomendaciones internacionales sobre evaluación de diferencias de color. Óptica Pura Y Aplicada 34:1–10.

Pasíes Oviedo, T. 2014. Los trabajos de conservación-restauración en el laboratorio del Museo de Prehistoria de Valencia: problemática de las antiguas intervenciones. ph investigación 3:1–19.

Plenderleith, H. J. 1967. La conservación de antigüedades y obras de arte. Insituto central de conservación y restauración de obras de arte, arqueología y etnología, Madrid, Spain, 423 pp.

Porto Tenreiro, Y. 2000. Medidas Urgentes de Conservación en Intervenciones Arqueológicas. Criterios e Convencións en Arqueoloxía da Paisaxe 13:5–35.

Rathgen, F. 1905. The Preservation of Antiquities: A Handbook for Curators. Cambridge University Press, Cambridge, UK, 202 pp.

Sease, C. 1994. A Conservation Manual for the Field Archaeologist. Cotsen Institute of Archaeology Press, Los Angeles, USA, 114 pp.

Stone, T. T., D. N. Dickel, and G. H. Doran. 1990. The preservation and conservation of waterlogged bone from the Windover Site, Florida: A comparison of methods. Journal of Field Archaeology 17:177–186.

STANDARDS CITED

ASTM D4303-03. Standard Test Methods for Lightfastness of Colorants Used in Artists materials. ASTM International, West Conshohocken, PA. 20. Available here: www.astm.org

UNE 48071:1982. Ensayo acelerado de amarilleo. Available here: www.aenor.es

UNE-EN 15886 :2011. Conservation of cultural property. Test methods. Color measurement of surfaces. Available here: www.aenor.es

APPENDIX I. GLASS SLIDE RESULTS

Table AI-1 - Yellowness Index of the vinyl resins, acrylic resins and Fluoline-A applied on glass slides, after heating in oven.

		YI	YF	ΔY	
RESIN	ACRONYM	x	x	x	δ
ACRIL 33	AC-33	-9,38	-9,08	0,30	0,14
EVALCITE 2044	EV-A	-9,51	-9,07	0,44	0,00
	EV-A+T	-9,52	-9,07	0,45	0,10
	EV-E	-9,54	-9,12	0,42	0,14
	EV-E+T	-9,52	-9,16	0,36	0,08
	EV-B	-9,51	-9,14	0,36	0,17
	EV-B+T	-9,46	-9,14	0,32	0,01
	EV-DW	-9,57	-9,00	0,56	0,01
	EV-D+T	-9,57	-9,11	0,46	0,06
P-B44	P44-A	-9,53	-9,67	-0,14	0,12
	P44-A+T	-9,57	-10,00	-0,43	0,28
	P44-A:A	-9,60	-8,27	1,33	0,52
	P44-A:A+T	-9,63	-8,78	0,85	0,39
	P44-EA	-9,58	-10,05	-0,47	0,02
	P44-EA+T	-9,53	-10,06	-0,53	0,06
	P44-B	-9,52	-10,03	-0,51	0,01
	P44-B+T	-9,57	-10,05	-0,49	0,16
	P44-DW	-9,59	-10,18	-0,59	0,00
	P44-DW+T	-9,56	-10,16	-0,60	0,06
P-B66	P66-A	-9,43	-9,70	-0,27	0,07
	P66-A+T	-9,40	-8,92	0,48	0,58
	P66-EA	-9,58	-10,12	-0,55	0,10
	P66-EA+T	-9,59	-10,12	-0,53	0,12
	P66-B	-9,47	-10,14	-0,67	0,08
	P66-B+T	-9,44	-10,07	-0,63	0,08
	P66-DW	-9,71	-10,06	-0,35	0,16
	P66-DW+T	-9,58	-10,04	-0,47	0,01
PB-72	P72-A	-9,38	-6,51	2,87	1,11
	P72-A+T	-9,55	-10,00	-0,45	0,08
	P72-A:A	-9,70	-7,38	2,32	0,21
	P72-A:A+T	-9,64	-9,80	-0,17	0,27
	P72-EA	-9,63	-10,15	-0,52	0,05
	P72-EA+T	-9,58	-10,03	-0,45	0,06
	P72-B	-9,58	-10,20	-0,62	0,08
	P72-B+T	-9,59	-10,23	-0,63	0,14
	P72-DW	-9,70	-10,00	-0,30	0,38
	P72-DW+T	-9,70	-10,23	-0,54	0,19

		YI	YF	ΔY	
RESIN	ACRONYM	x	x	x	δ
P-B82	P82-A	-9,46	-5,73	3,73	0,38
	P82-A+T	-9,49	-10,09	-0,60	0,03
	P82-A:A	-9,41	-8,81	0,60	0,23
	P82-A:A+T	-9,61	-10,12	-0,51	0,15
	P82-1:9	-9,96	-10,22	-0,26	0,14
	P82-1:9+T	-10,07	-9,99	0,08	0,57
	P82-EA	-9,52	-10,18	-0,66	0,03
	P82-EA+T	-9,43	-10,18	-0,75	0,07
	P82-B	-9,39	-10,09	-0,70	0,11
	P82-B+T	-9,41	-10,19	-0,78	0,16
	P82-DW	-9,57	-10,23	-0,65	0,15
	P82-DW+T	-9,58	-10,22	-0,64	0,01
P-B72+44 50%	P50%-A	-9,56	-9,34	0,22	0,02
	P50%-A+T	-9,59	-9,32	0,27	0,08
	P50%-A:A	-9,60	-9,19	0,42	0,09
	P50%-A:A+T	-9,64	-8,96	0,68	0,01
	P50%-EA	-9,58	-9,35	0,24	0,07
	P50%-EA+T	-9,52	-9,28	0,24	0,06
	P50%-B	-9,48	-9,31	0,17	0,13
	P50%-B+T	-9,51	-9,31	0,19	0,10
	P50%-DW	-9,53	-9,42	0,11	0,12
	P50%-DW+T	-9,55	-9,41	0,14	0,02
VINNAPAS LEF10	VN	-9,42	-8,91	0,51	0,06
MOWITAL B60 HH	MW	-9,64	-8,04	1,60	0,24
	MW+T	-9,67	-8,64	1,03	0,08
K60	K-A	-9,52	-9,24	0,28	0,01
	K-A+T	-9,56	-9,33	0,23	0,02
	K-A:A	-9,50	-9,36	0,14	0,23
	K-A:A+T	-9,59	-9,42	0,18	0,16
	K-E	-9,31	-9,26	0,05	0,03
	K-E+T	-9,38	-9,29	0,09	0,07
	K-B	-9,55	-9,32	0,24	0,09
	K-B+T	-9,53	-9,37	0,16	0,03
	K-DW	-9,59	-9,34	0,25	0,04
	K-DW+T	-9,69	-9,35	0,34	0,06
FLUOLINE A	FA-A	-9,34	-9,70	-0,36	0,06

Table AI-2. Increments results of the vinyl resins, acrylic resins and Fluoline-A applied on glass slides, after exposure of 240h to UV.

RESIN	ACRONYM	ΔL*	ΔE00	ΔC*	Δhº
ACRIL 33	AC-33	-0,2	0,17	0,16	0,02
EVALCITE 2044	EV-A	-0,47	0,32	0,21	0,15
	EV-A+T	-0,37	0,26	0,18	0,11
	EV-E	-0,37	0,26	0,19	0,03
	EV-E+T	-0,3	0,22	0,17	-0,04
	EV-B	-0,35	0,27	0,23	0,02
	EV-B+T	-0,27	0,23	0,22	-0,02
	EV-DW	-0,38	0,25	0,14	0,03
	EV-D+T	-0,32	0,24	0,2	0,08
P-B44	P44-A	0,1	0,08	-0,07	-0,01
	P44-A+T	-0,05	0,1	-0,12	0,13
	P44-A:A	0,19	0,13	-0,21	0,13
	P44-A:A+T	1,08	0,83	-0,2	-0,17
	P44-EA	-0,05	0,16	0,03	0,23
	P44-EA+T	-0,11	0,17	0,71	0,28
	P44-B	-0,15	0,19	-0,2	0,4
	P44-B+T	-0,18	0,19	-0,19	0,36
	P44-DW	-0,24	0,26	-0,3	0,31
	P44-DW+T	-0,21	0,21	-0,21	0,39
P-B66	P66-A	-0,13	0,12	-0,32	0,24
	P66-A+T	0,18	0,13	-0,26	-0,02
	P66-EA	-0,33	0,31	-0,21	0,34
	P66-EA+T	-0,25	0,25	-0,23	0,4
	P66-B	-0,29	0,25	-0,1	0,36
	P66-B+T	-0,13	0,16	0,11	0,32
	P66-DW	-0,17	0,19	-0,22	0,36
	P66-DW+T	-0,2	0,21	-0,17	0,31
PB-72	P72-A	0,92	0,67	0,45	-0,79
	P72-A+T	-0,14	0,14	-0,14	0,26
	P72-A:A	0,39	0,24	-0,27	-0,16
	P72-A:A+T	0,59	0,36	-0,16	0,06
	P72-EA	0	0,12	0	0,26
	P72-EA+T	-0,24	0,25	-0,2	0,32
	P72-B	-0,07	0,17	-0,22	0,3
	P72-B+T	-0,19	0,2	-0,22	0,3
	P72-DW	0,18	0,12	0,03	0,19
	P72-DW+T	-0,13	0,18	0,05	0,31

RESIN	ACRONYM	ΔL*	ΔE00	ΔC*	Δhº
P-B82	P82-A	0,44	0,27	0,04	-0,14
	P82-A+T	-0,17	0,18	-0,2	0,17
	P82-A:A	1,15	0,72	0,13	-0,25
	P82-A:A+T	0,09	0,14	-0,17	0,11
	P82-1:9	-0,13	0,12	-0,07	0,31
	P82-1:9+T	0,69	0,46	0,2	0,18
	P82-EA	0,17	0,11	-0,03	0,06
	P82-EA+T	-0,36	0,31	-0,29	0,31
	P82-B	-0,02	0,11	-0,15	0,21
	P82-B+T	-0,22	0,24	-0,28	0,23
	P82-DW	-0,1	0,15	-0,19	0,13
	P82-DW+T	-0,13	0,18	-0,22	0,2
P-B72+44 50%	P50%-A	-0,26	0,19	0,14	-0,2
	P50%-A+T	-0,25	0,19	0,17	-0,09
	P50%-A:A	-0,03	0,21	0,12	-0,17
	P50%-A:A+T	0,04	0,28	0,19	-0,22
	P50%-EA	-0,34	0,23	0,15	0,01
	P50%-EA+T	-0,25	0,2	0,16	0,01
	P50%-B	-0,23	0,18	0,13	-0,01
	P50%-B+T	-0,24	0,18	0,12	0,05
	P50%-DW	-0,27	0,19	0,3	0,01
	P50%-DW+T	-0,28	0,19	0,39	-0,02
VINNAPAS LEF10	VN	-0,1	0,21	0,28	-0,23
MOWITAL B60 HH	MW	-1,05	0,67	0,04	-0,09
	MW+T	-1,14	0,72	-0,01	0,03
K60	K-A	-0,31	0,24	0,2	0,09
	K-A+T	-0,7	0,43	0,06	0,18
	K-A:A	-0,24	0,16	0,09	0,11
	K-E	-0,48	0,3	0,09	0,11
	K-E+T	-0,86	0,53	0,07	0,28
	K-B	-0,27	0,21	0,18	0,04
	K-B+T	-0,79	0,49	0,12	0,15
	K-DW	-0,15	0,2	0,25	-0,04
	K-DW+T	-0,3	0,25	0,23	-0,13
FLUOLINE A	FA-A	-0,15	0,14	-0,1	0,35

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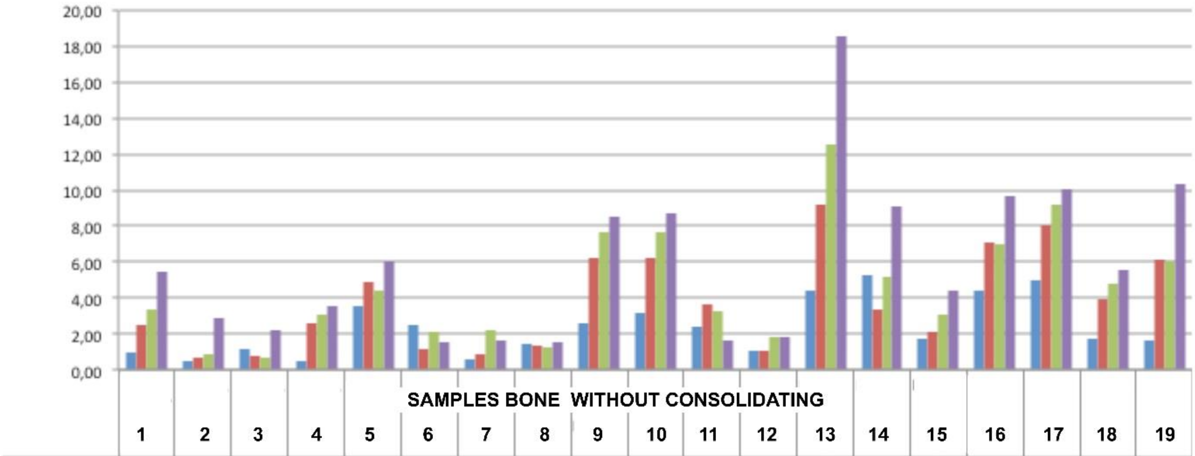
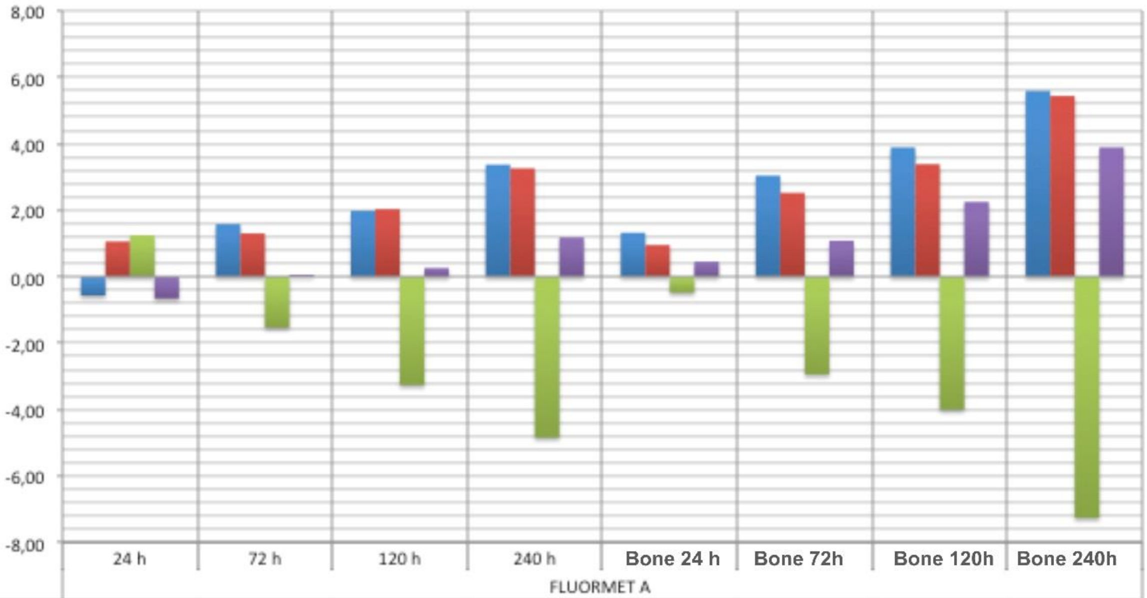
APPENDIX II. CONSOLIDATION BONE MATERIAL, CIELCH DIAGRAMS



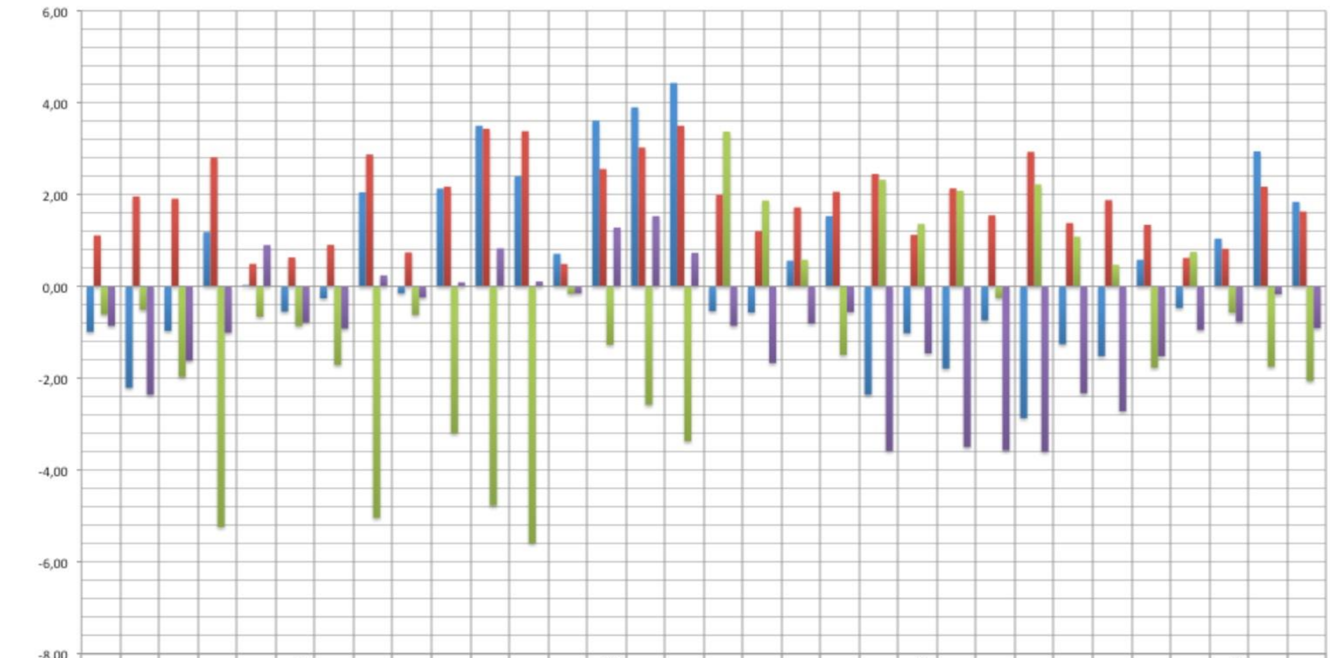
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
ΔE* ab 24H	0,95	0,49	1,18	0,49	3,55	2,45	0,62	1,48	2,63	3,13	2,4	1,04	4,39	5,23	1,73	4,40	4,99	1,71	1,64
ΔE* ab 72H	2,52	0,63	0,79	2,56	4,86	1,12	0,82	1,33	6,23	6,25	3,7	1,03	9,20	3,34	2,10	7,05	8,01	3,90	6,10
ΔE* ab 120H	3,39	0,90	0,70	3,02	4,45	2,13	2,17	1,24	7,63	7,70	3,3	1,79	12,55	5,14	3,07	6,95	9,21	4,79	6,01
ΔE* ab 240H	5,44	2,87	2,24	3,50	6,06	1,55	1,63	1,55	8,49	8,73	1,7	1,81	18,61	9,13	4,45	9,65	10,08	5,54	10,33

Figure AII-1 - Changes produced in bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	24 h	72 h	120 h	240 h	Bone 24 h	Bone 72h	Bone 120h	Bone 240h
ΔL*	-0,57	1,58	1,98	3,37	1,32	3,04	3,89	5,59
ΔE00* ab	1,06	1,30	2,03	3,26	0,95	2,52	3,39	5,44
ΔC*	1,24	-1,53	-3,26	-4,84	-0,48	-2,94	-4,00	-7,26
Δhº	-0,66	0,05	0,26	1,18	0,45	1,08	2,25	3,89

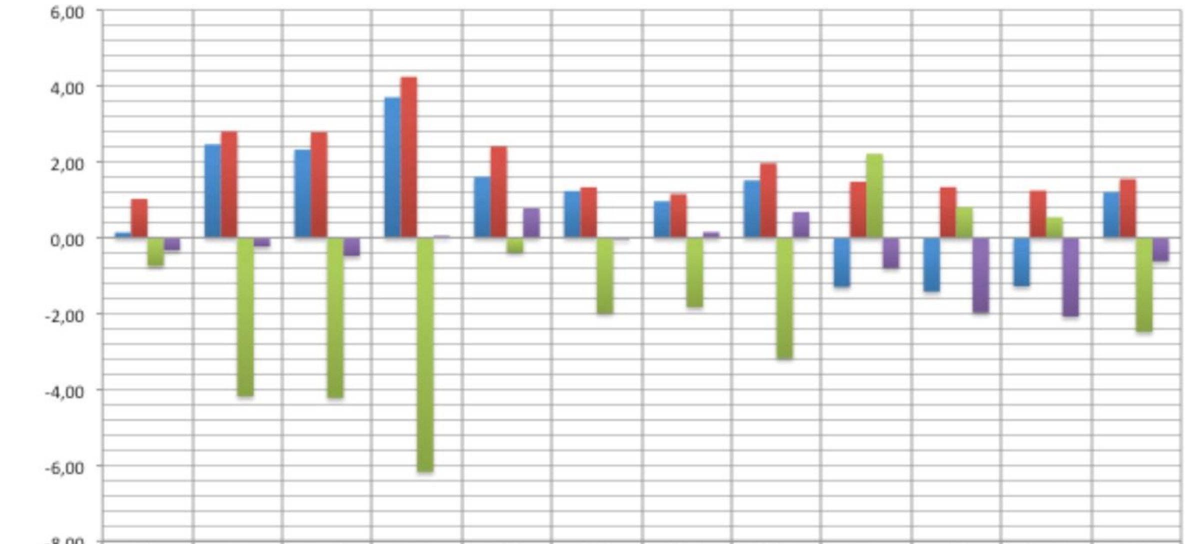
Figure AII-2 - Changes produced in areas treated with Fluoline-A on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	EVALCITE ACETONA 24 h	72 h	120 h	240 h	Bone 24h	Bone 72 h	Bone 120 h	Bone 240 h	EVALCITE ETIL ACET 24 h	72 h	120 h	240 h	Bone 24h	Bone 72 h	Bone 120 h	Bone 240 h
ΔL*	-0,99	-2,21	-0,97	1,18	0,02	-0,55	-0,26	2,05	-0,15	2,13	3,50	2,40	0,71	3,61	3,90	4,43
ΔE00* ab	1,11	1,96	1,91	2,81	0,49	0,63	0,90	2,87	0,74	2,17	3,43	3,38	0,49	2,56	3,02	3,50
ΔC*	-0,61	-0,51	-1,97	-5,24	-0,66	-0,86	-1,71	-5,04	-0,62	-3,20	-4,77	-5,59	-0,16	-1,27	-2,58	-3,37
Δhº	-0,86	-2,36	-1,62	-1,01	0,90	-0,78	-0,92	0,24	-0,24	0,09	0,83	0,11	-0,15	1,28	1,53	0,73

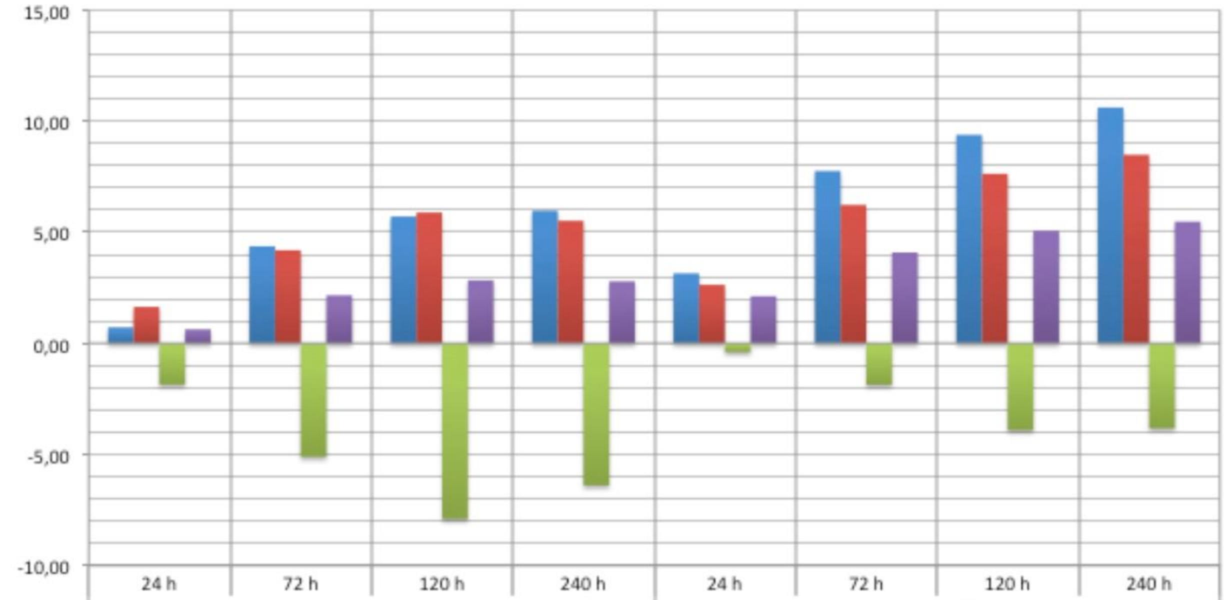
	EVALCITE BUTIL ACET 24 h	72 h	120 h	240 h	Bone 24h	Bone 72 h	Bone 120 h	Bone 240 h	EVALCITE DW 24 h	72 h	120 h	240 h	Bone 24h	Bone 72 h	Bone 120 h	Bone 240 h
ΔL*	-0,54	-0,57	0,56	1,53	-2,36	-1,02	-1,79	-0,74	-2,87	-1,26	-1,52	0,58	-0,47	1,04	2,94	1,84
ΔE00* ab	1,99	1,20	1,72	2,06	2,45	1,12	2,13	1,55	2,93	1,38	1,88	1,34	0,62	0,82	2,17	1,63
ΔC*	3,37	1,87	0,58	-1,49	2,32	1,36	2,08	-0,25	2,22	1,08	0,47	-1,77	0,75	-0,57	-1,75	-2,06
Δhº	-0,86	-1,67	-0,81	-0,56	-3,58	-1,46	-3,50	-3,57	-3,60	-2,33	-2,72	-1,52	-0,95	-0,77	-0,17	-0,91

Figure AII-3 - Changes produced in areas treated with Evalcite® on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



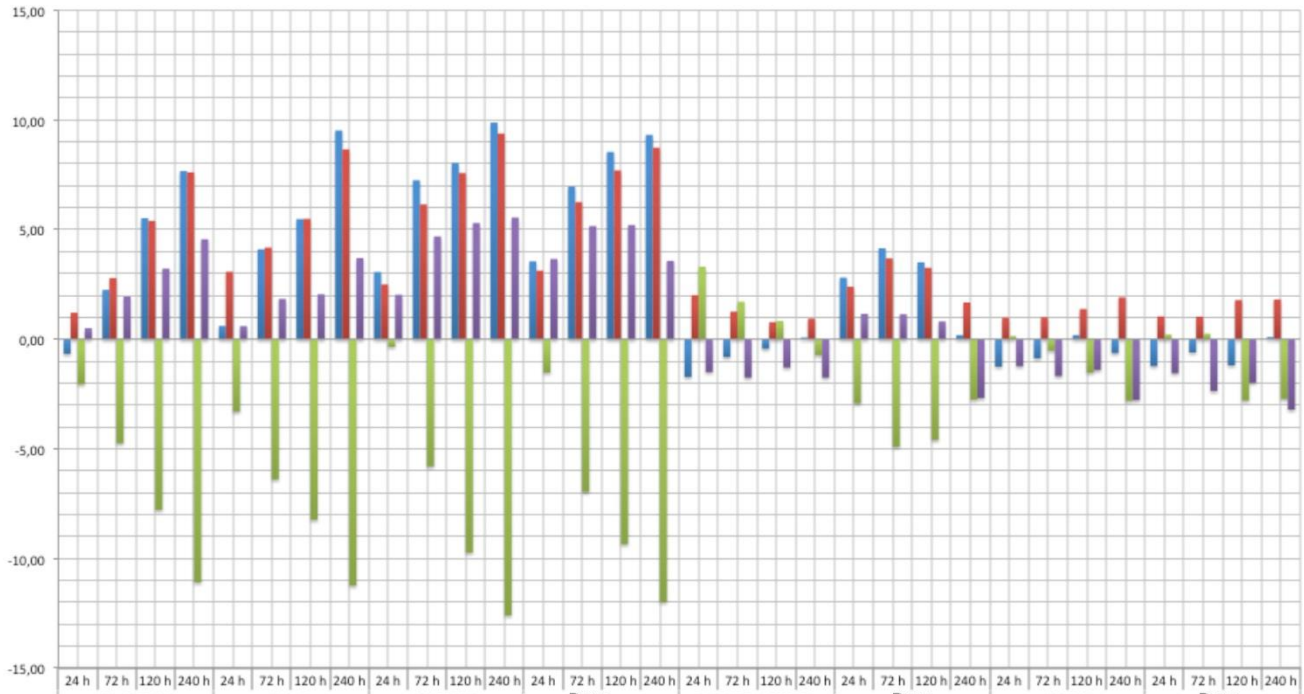
	ACRIL 33 24 h	ACRIL 33 72 h	ACRIL 33 120 h	ACRIL 33 240 h	VINNAPAS LEF10 24 h	VINNAPAS LEF10 72 h	VINNAPAS LEF10 120 h	VINNAPAS LEF10 240 h	BONE MATERIAL 24 h	BONE MATERIAL 72 h	BONE MATERIAL 120 h	BONE MATERIAL 240 h
ΔL*	0,14	2,46	2,32	3,70	1,60	1,23	0,96	1,51	-1,30	-1,42	-1,28	1,20
ΔE00* ab	1,02	2,80	2,78	4,24	2,41	1,33	1,15	1,96	1,48	1,33	1,24	1,55
ΔC*	-0,74	-4,18	-4,22	-6,17	-0,38	-1,98	-1,83	-3,17	2,21	0,80	0,54	-2,48
Δhº	-0,33	-0,23	-0,48	0,04	0,77	-0,05	0,15	0,68	-0,80	-1,97	-2,08	-0,62

Figure AII-4 - Changes produced in areas treated with emulsions resins (acril-33 and Vinnapas® LEF10) on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
	MOWITAL				BONE MATERIAL			
ΔL*	0,72	4,37	5,71	5,97	3,15	7,76	9,39	10,62
ΔE00* ab	1,64	4,19	5,89	5,52	2,63	6,23	7,63	8,49
ΔC*	-1,86	-5,11	-7,91	-6,40	-0,39	-1,87	-3,91	-3,83
Δhº	0,63	2,16	2,84	2,79	2,12	4,09	5,07	5,48

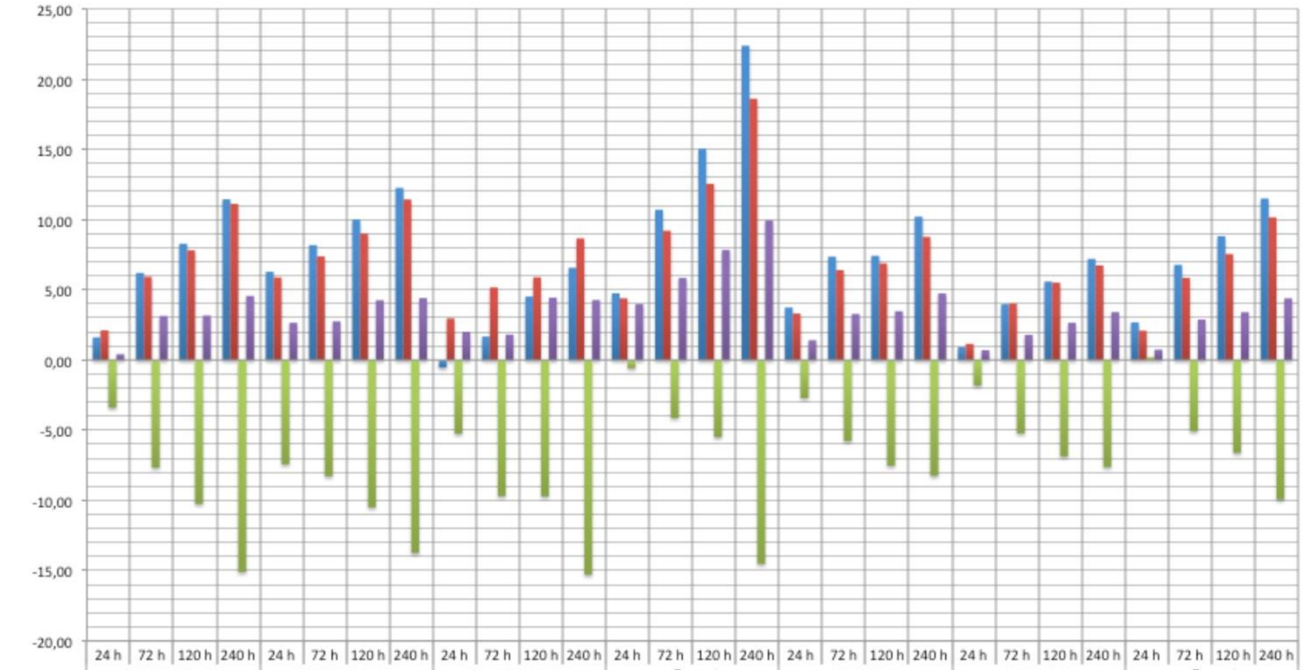
Figure AII-5 - Changes produced in areas treated with Mowital® on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
	K60 ACETONA				K60 A:A				K60 ETANOL				Bone			
ΔL*	-0,66	2,25	5,52	7,67	0,61	4,10	5,48	9,52	3,07	7,25	8,04	9,88	3,55	6,96	8,54	9,32
ΔE00* ab	1,21	2,79	5,40	7,61	3,08	4,18	5,49	8,66	2,50	6,15	7,58	9,38	3,13	6,25	7,70	8,73
ΔC*	-2,05	-4,74	-7,78	-11,09	-3,30	-6,39	-8,23	-11,23	-0,34	-5,80	-9,73	-12,59	-1,52	-6,96	-9,35	-11,98
Δhº	0,50	1,94	3,22	4,56	0,60	1,84	2,05	3,70	2,03	4,69	5,30	5,55	3,66	5,16	5,21	3,57

	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
	K60 BUTIL ACETATO				Bone				K60 DW				Bone			
ΔL*	-1,72	-0,81	-0,43	0,08	2,81	4,15	3,51	0,19	-1,25	-0,87	0,19	-0,63	-1,22	-0,60	-1,19	0,10
ΔE00* ab	2,01	1,26	0,78	0,94	2,4	3,7	3,3	1,7	0,98	1,00	1,38	1,91	1,04	1,03	1,79	1,81
ΔC*	3,31	1,71	0,83	-0,72	-2,92	-4,90	-4,59	-2,75	0,15	-0,52	-1,52	-2,80	0,22	0,26	-2,79	-2,72
Δhº	-1,50	-1,75	-1,29	-1,75	1,16	1,14	0,81	-2,68	-1,23	-1,68	-1,40	-2,77	-1,55	-2,36	-1,97	-3,21

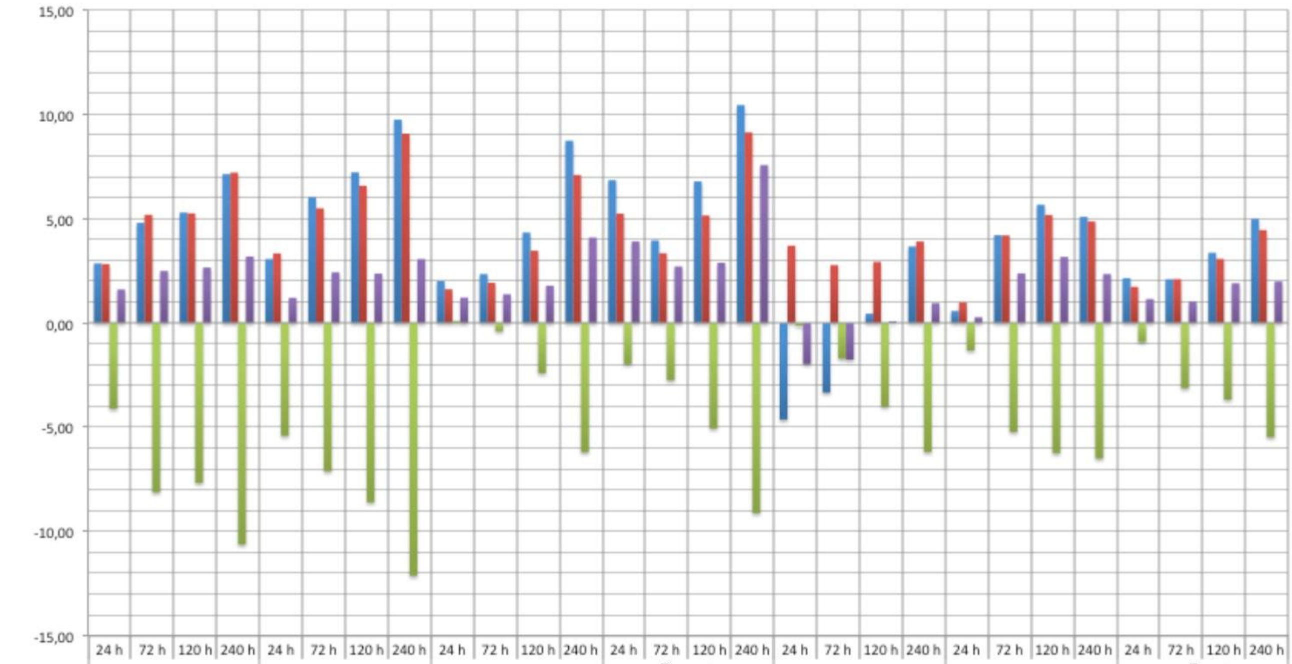
Figure AII-6 - Changes produced in areas treated with K60 on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	P50% ACETONA				P50% ETIL ACET				P50% BUTIL ACET			
	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
ΔL*	1,61	6,20	8,28	11,44	6,28	8,18	10,00	12,26	-0,53	1,67	4,52	6,57
ΔE00* ab	2,11	5,92	7,81	11,12	5,88	7,38	9,00	11,43	2,96	5,17	5,89	8,66
ΔC*	-3,39	-7,66	-10,25	-15,10	-7,42	-8,27	-10,49	-13,74	-5,24	-9,69	-9,71	-15,28
Δhº	0,42	3,14	3,17	4,56	2,65	2,75	4,26	4,41	2,01	1,81	4,44	4,27

	Bone				P50% DW				P50%-A:A				Bone			
	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
ΔL*	4,75	10,70	15,04	22,38	3,74	7,36	7,42	10,21	0,91	3,97	5,59	7,20	2,68	6,78	8,82	11,50
ΔE00* ab	4,39	9,20	12,55	18,61	3,31	6,40	6,88	8,77	1,15	4,02	5,51	6,73	2,09	5,85	7,55	10,16
ΔC*	-0,58	-4,12	-5,48	-14,52	-2,71	-5,77	-7,53	-8,24	-1,81	-5,22	-6,86	-7,62	0,21	-5,06	-6,61	-9,92
Δhº	3,97	5,84	7,84	9,94	1,41	3,28	3,47	4,74	0,70	1,79	2,65	3,41	0,74	2,88	3,40	4,39

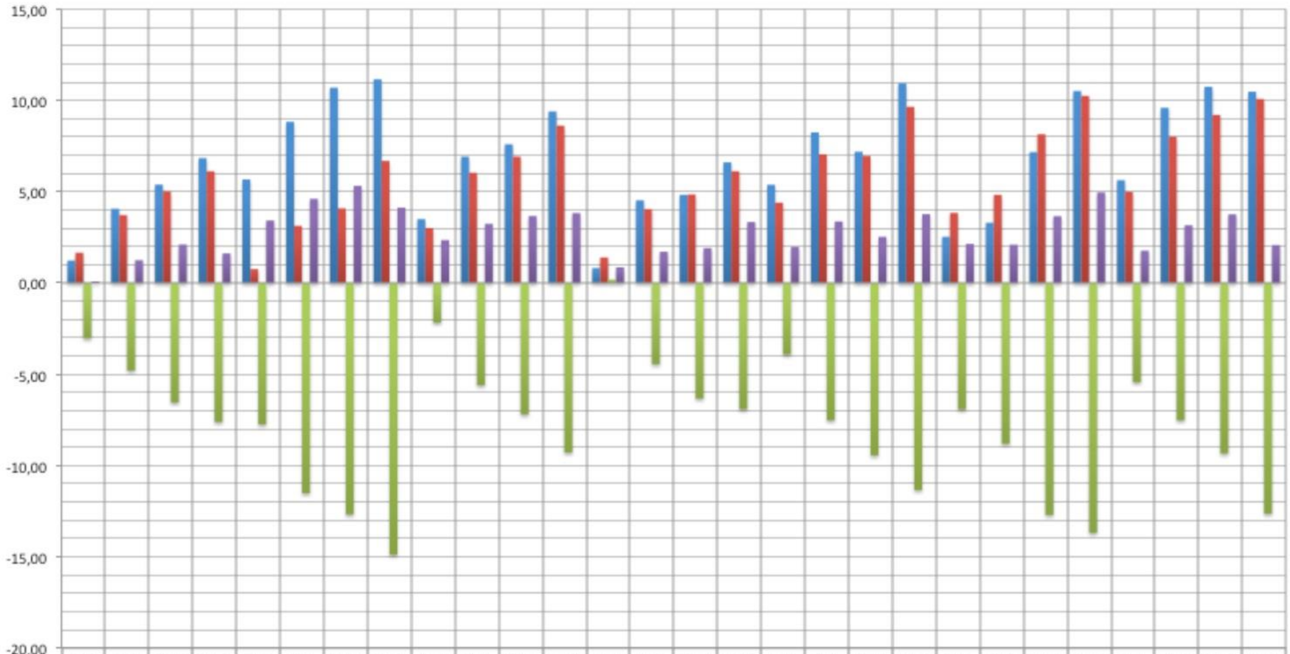
Figure AII-7 - Changes produced in areas treated with Paraloid™ B72 + 44 on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	P44 ACETONA				P44 ETIL ACET				P44-A:A			
	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
ΔL*	2,85	4,79	5,29	7,13	3,06	6,02	7,21	9,74	2,00	2,34	4,33	8,73
ΔE00* ab	2,82	5,18	5,25	7,20	3,33	5,49	6,57	9,07	1,61	1,92	3,46	7,09
ΔC*	-4,11	-8,12	-7,67	-10,62	-5,41	-7,11	-8,60	-12,12	0,10	-0,40	-2,41	-6,20
Δhº	1,60	2,49	2,65	3,18	1,20	2,42	2,36	3,06	1,21	1,37	1,78	4,09

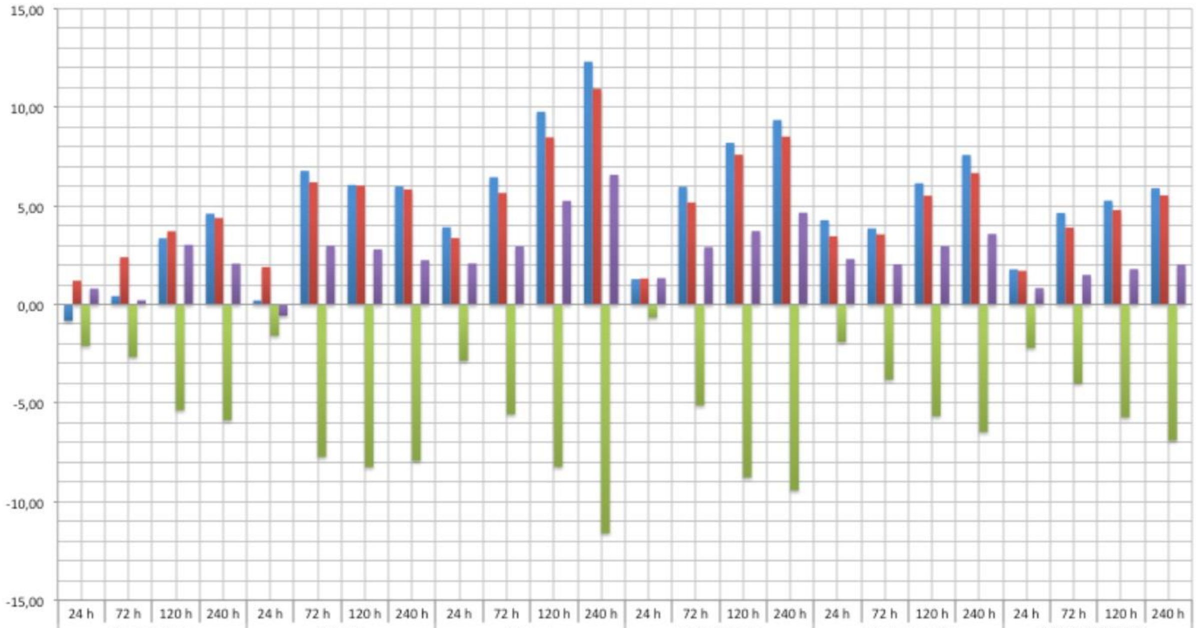
	Bone				P44 BUTIL ACET				P44-DW				Bone			
	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
ΔL*	6,84	3,95	6,78	10,44	-4,64	-3,34	0,44	3,66	0,57	4,20	5,66	5,08	2,14	2,09	3,36	4,98
ΔE00* ab	5,23	3,34	5,14	9,13	3,70	2,77	2,92	3,90	0,98	4,19	5,17	4,86	1,73	2,10	3,07	4,45
ΔC*	-1,97	-2,75	-5,06	-9,12	-0,14	-1,71	-4,01	-6,19	-1,32	-5,23	-6,24	-6,50	-0,91	-3,13	-3,68	-5,48
Δhº	3,90	2,70	2,88	7,56	-1,97	-1,76	0,05	0,94	0,27	2,37	3,16	2,34	1,14	1,02	1,90	1,98

Figure AII-8 - Changes produced in areas treated with Paraloid™ B-44 on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



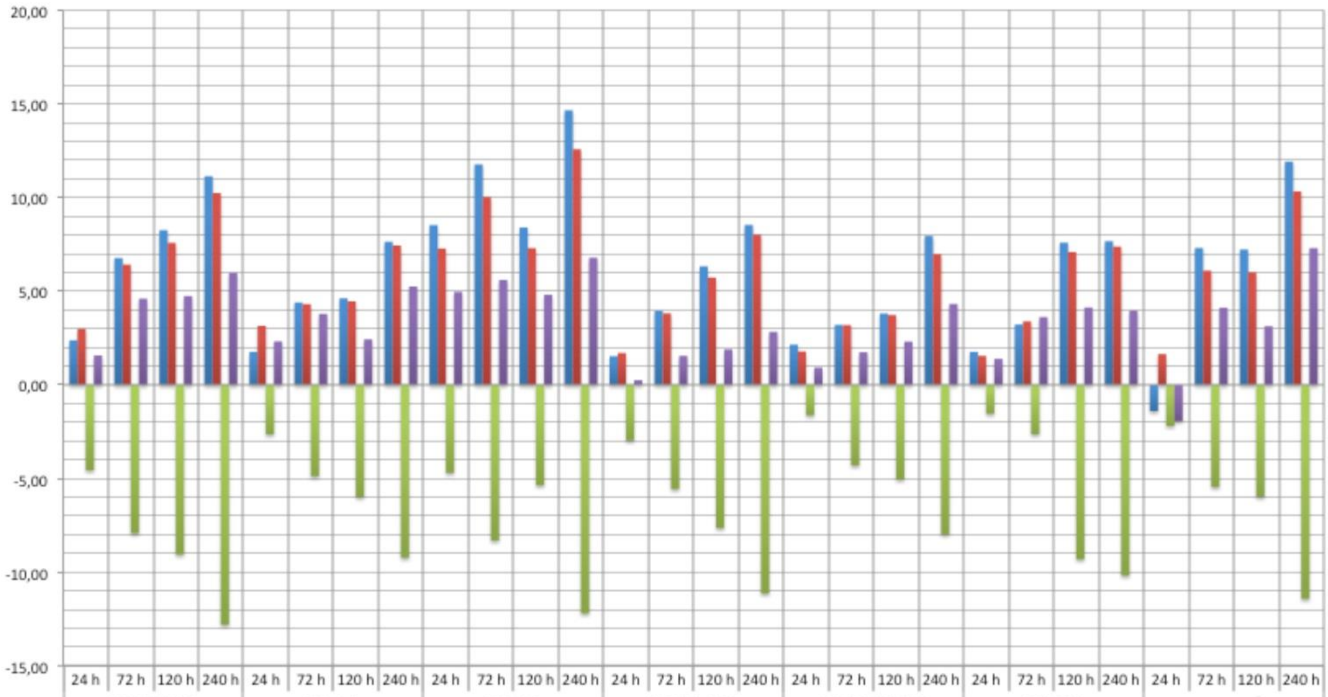
	P72 ACETONA				P72 ETILL ACET				P72-DW				P72 BUTIL ACET				Bone				P72-A:A				Bone			
	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
ΔL*	1,23	4,07	5,39	6,84	5,67	8,83	10,70	11,16	3,50	6,92	7,60	9,40	0,82	4,53	4,83	6,61	5,38	8,25	7,19	10,94	2,53	3,30	7,17	10,52	5,63	9,60	10,75	10,48
ΔE00* ab	1,66	3,72	5,02	6,12	0,76	3,13	4,09	6,69	3,01	6,04	6,92	8,62	1,40	4,05	4,85	6,12	4,40	7,05	6,95	9,65	3,84	4,83	8,15	10,25	4,99	8,01	9,21	10,08
ΔC*	-3,03	-4,80	-6,55	-7,62	-7,75	-11,52	-12,68	-14,89	-2,17	-5,60	-7,20	-9,29	0,19	-4,45	-6,33	-6,92	-3,91	-7,52	-9,44	-11,34	-6,93	-8,81	-12,71	-13,69	-5,44	-7,52	-9,34	-12,64
Δhº	0,06	1,25	2,11	1,62	3,42	4,61	5,32	4,13	2,35	3,24	3,67	3,83	0,86	1,71	1,91	3,34	1,97	3,37	2,53	3,77	2,14	2,10	3,66	4,96	1,77	3,16	3,76	2,08

Figure AII-9 - Changes produced in areas treated with Paraloid™ B-72 on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	P66 ETIL ACET				P66-DW				P66-A:A				P66 ACETONA				P66 BUTIL ACET				BONE MATERIAL			
	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
ΔL*	-0,83	0,43	3,36	4,61	0,21	6,78	6,07	5,99	3,92	6,46	9,78	12,32	1,29	5,97	8,20	9,36	4,28	3,86	6,15	7,59	1,78	4,65	5,27	5,90
ΔE00* ab	1,21	2,40	3,72	4,39	1,90	6,20	6,03	5,84	3,37	5,66	8,48	10,94	1,32	5,18	7,60	8,52	3,46	3,56	5,52	6,67	1,71	3,90	4,79	5,54
ΔC*	-2,10	-2,66	-5,36	-5,87	-1,58	-7,73	-8,25	-7,93	-2,85	-5,57	-8,24	-11,61	-0,66	-5,12	-8,77	-9,43	-1,90	-3,81	-5,66	-6,47	-2,20	-3,99	-5,72	-6,90
Δhº	0,81	0,22	3,03	2,08	-0,57	2,98	2,80	2,25	2,09	2,95	5,26	6,58	1,34	2,91	3,73	4,66	2,31	2,04	2,96	3,58	0,83	1,50	1,80	2,03

Figure AII-10 - Changes produced in areas treated with Paraloid™ B-66 on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.



	P82 ACETONA				P82-A:A				P82-1:9				P82 ETIL ACET				P82 BUTIL ACET				P82-DW				BONE MATERIAL			
	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h	24 h	72 h	120 h	240 h
ΔL*	2,38	6,77	8,26	11,14	1,76	4,40	4,62	7,64	8,53	11,77	8,40	14,66	1,53	3,95	6,33	8,54	2,15	3,20	3,81	7,95	1,76	3,22	7,59	7,67	-1,40	7,31	7,23	11,92
ΔE00* ab	2,99	6,42	7,58	10,24	3,15	4,31	4,46	7,44	7,28	10,03	7,30	12,58	1,70	3,82	5,72	8,02	1,78	3,19	3,73	6,98	1,55	3,39	7,09	7,38	1,64	6,10	6,01	10,33
ΔC*	-4,56	-7,92	-9,06	-12,81	-2,64	-4,88	-5,99	-9,23	-4,70	-8,31	-5,36	-12,20	-2,96	-5,56	-7,64	-11,14	-1,62	-4,30	-5,05	-7,98	-1,54	-2,64	-9,31	-10,18	-2,19	-5,45	-5,98	-11,42
Δhº	1,57	4,60	4,74	5,98	2,32	3,79	2,43	5,25	4,96	5,60	4,81	6,79	0,25	1,55	1,89	2,83	0,92	1,74	2,31	4,32	1,39	3,62	4,13	3,96	-1,92	4,12	3,13	7,30

Figure AII-11 - Changes produced in areas treated with Paraloid™ B-82 on bone material. Increments L*, E00, C* an hº after exposure of 240 h to UV radiation.

APPENDIX III. RESULTS. SUMMARY TABLE

Table AIII-1 - Changes observed on consolidated surfaces.

					GLAS SLIDE		BONE				
RESIN	NAME	SOLVENT	% (W/V)	APLICATION	ΔIY	ΔE00	ΔE00	ΔL*	COMPARISION TO BONE MATERIAL	VISUAL EVALUATION	RECOMMENDED
VINIL RESINS	VINNAPAS LEF 10W	DEIONIZED WATER	5	HOMOGENEOUS BRIGHTNESS	0,51	0,21	1,96	1,51	SIMILAR BEHAVIOR. A LITTLE ALTERED	GENERAL APPEARANCE: HOMOGENEOUS AGING	TO BONE DAMP
	MOWITAL B60HH	ETHYL ALCOHOL	3	NO DIFFERENCE	1,60	0,67	5,52	5,97	BETTER BEHAVIOR THAN BONE: MUCH DIFFERENCE	GENERAL APPEARANCE: HOMOGENEOUS AGING	NO
	K 60	ETHYL ALCOHOL	3	NO DIFFERENCE	0,05	0,3	9,38	9,88	MORE ALTERED	GENERAL APPEARANCE: HOMOGENEOUS AGING	YES
		ACETONE	3	BRIGHTNESS	0,28	0,24	7,61	7,67			NO
		ACETONE:ETHYL ALCOHOL (1:1)	3	BRIGHTNESS	0,14	0,16	8,66	9,52			NO
		BUTYL ACETATE	3	BRIGHTNESS	0,24	0,21	0,94	0,08	BETTER BEHAVIOR THAN BONE: MUCH DIFFERENCE		NO
		DOWANOL PM	3	BRIGHTNESS	0,25	0,2	1,91	-0,6			NO
OTHER	FLUOLINE A	ACETONE	15	NO DIFFERENCE	-0,36	0,14	3,26	3,37	LESS ALTERATION		YES
ACRYL RESINS	Acril®-33	DEIONIZED WATER	5	HOMOGENEOUS BRIGHTNESS	0,30	0,17	4,24	3,7	MORE ALTERED	GENERAL APPEARANCE: HOMOGENEOUS AGING	BONE DAMP
	EVALCITE 2044	ACETONE	5	BRIGHTNESS	0,44	0,32	2,81	1,18	MORE ALTERED	GENERAL APPEARANCE: HOMOGENEOUS AGING	NO
		ETHYL ACETATE	5	NO DIFFERENCE	0,42	0,26	3,38	2,4	LESS WHITNESS THAN UNTREATED SURFACE		NO
		BUTYL ACETATE	5	NO DIFFERENCE	0,36	0,27	2,06	1,53	LESS ALTERATION		NO
		DOWANOL PM	5	NO DIFFERENCE	0,56	0,25	1,34	0,58	LESS ALTERATION		NO
	PARALOID B-44	ACETONE	5	BRIGHTNESS	-0,14	0,08	7,2	7,13	MORE ALTERED	GENERAL BEHAVIOR: MAJOR ALTERATION IN THE TREATED AREA	NO
		ACETONE:ETHYL ALCOHOL (1:1)	5	WHITE VEIL	-	-	.	-	-		NO
		ETHYL ACETATE	5	BRIGHTNESS	-0,47	0,16	9,07	9,74	MORE ALTERED		NO
		BUTYL ACETATE	5	BRIGHTNESS	-0,51	0,19	3,9	3,66	DIFERENT BEHAVIOR		NO
		DOWANOL PM	5	BRIGHTNESS	-0,59	0,26	4,86	5,08	SIMILAR BEHAVIOR		NO
	PARALOID B-66	ACETONE	5	VERY BRIGHT	-0,27	0,12	8,52	9,36	MORE ALTERED	GENERAL BEHAVIOR: MAJOR ALTERATION IN THE TREATED AREA	NO
		ACETONE:ETHYL ALCOHOL (1:1)	5	WHITE VEIL	-	-	-	-	-		NO
		ETHYL ACETATE	5	HOMOGENEOUS BRIGHTNESS	-0,55	0,31	4,39	4,61	GOOD RESULT		NO
		BUTYL ACETATE	5	VERY BRIGHT	-0,67	0,25	6,67	7,59	MORE ALTERED		NO
		DOWANOL PM	5	HOMOGENEOUS BRIGHTNESS	-0,35	0,19	6,03	6,07	SIMILAR BEHAVIOR		YES
	PARALOID B-82	ACETONE	5	VERY BRIGHT	3,73	0,27	10,24	11,4	SIMILAR BEHAVIOR	GENERAL BEHAVIOR: MAJOR ALTERATION IN THE TREATED AREA	NO
		ACETONE:ETHYL ALCOHOL (1:1)	5	WHITE VEIL	-	-	-	-	-		NO
		WATER: ETHYL ALCOHOL (1:9)	5	WHITE VEIL	-	-	-	-	-		NO
		ETHYL ACETATE	5	BRIGHTNESS	-0,66	0,11	8,02	8,54	LITTLE DIFFERENCE TO THE BONE MATERIAL		NO
		BUTYL ACETATE	5	NO DIFFERENCE	-0,70	0,11	6,98	7,95			
		DOWANOL PM	5	NO DIFFERENCE	-0,65	0,15	7,38	7,36			
	PARALOID B-72	ACETONE	5	BRIGHTNESS	2,87	0,67	6,12	6,84	MORE ALTERED	GENERAL APPEARANCE: BONE MORE ALRERATION	NO
		ACETONE:ETHYL ALCOHOL (1:1)	5	WHITE VEIL	-	-	-	-	-		YES
		ETHYL ACETATE	5	BRIGHTNESS	-0,52	0,12	6,69	11,2	MORE ALTERED		NO
		BUTYL ACETATE	5	BRIGHTNESS	-0,62	0,17	6,12	6,61	MORE STABLE		YES
		DOWANOL PM	5	BRIGHTNESS	-0,30	0,12	8,62	9,4	SIMILAR BEHAVIOR. A LITTLE ALTERED		YES
	PARALOID B-72+ 44	ACETONE	5	BRIGHTNESS	0,22	0,19	11,12	1,44	LESS ALTERATION	GENERAL APPEARANCE: HOMOGENEOUS AGING	NO
		ACETONE:ETHYL ALCOHOL (1:1)	5	WHITE VEIL	-	-	-	-	-		NO
		ETHYL ACETATE	5	BRIGHTNESS	0,24	0,23	12,16	11,4	LESS ALTERATION		NO
		BUTYL ACETATE	5	NO DIFFERENCE	0,17	0,18	5,89	8,66			YES
		DOWANOL PM	5	NO DIFFERENCE	0,11	0,19	8,77	10,2			YES

NOTE: VINNAPASS LEF 10W (synthetic dispersion based on an ethylene, vinyl acetate and vinyl chloride thermopolymer); **Mowital B60HH** (Vinyl buyral polymer); **K60** (PVA, thermoplastic resin based on polyvinyl acetate homopolymers); **FLUOLINE A** (FLUORMET A, based on fluorelastomers and acrylic polymers, in acetone); **ACRIL 33** (aqueous dispersion); **EVALCITE 2044** (Butyl methacrylate); **PARALOID B-44** (Methyl methacrylate); **PARALOID B-66** (Methyl Buthyl Methacrylate); **PARALOID B-82** (Methyl Methacrylate); **PARALOID B-72** (Ethyl Methacrylate).

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CONSERVATION-RESTORATION APPLIED TO A FOSSIL ADHERED TO A SPELEOTHEM (MIDDLE PLEISTOCENE) FROM POSTES CAVE (FUENTES DE LEÓN, SPAIN)

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ABSTRACT

The conservation-restoration methodology used on most Middle Pleistocene layers from the Postes Cave site fossils is minimal intervention. The fossils from Stratigraphic Unit Pleistocene 1 layer are covered by a 0,3 m-thick speleothem around the bones.
This work describes four restoration treatments applied to one of the fossils from this layer since its discovery, to reverse fossil deterioration and/or total or partial loss. To extract the bone it was necessary to hit the speleothem and fracture it, damaging and breaking the fossil into small fragments. These treatments consisted in the application of a bandage *in situ,* removal of the bandage, cleaning, consolidation and reconstruction in the research laboratory.
We have recovered and stabilized the fossil so we can take, touch and move them to carry out a taxonomic study. These studies have resulted in the identification of the fossil as an *Ursus arctos* tibia.

Keywords: fossil; Middle Pleistocene; restoration; reconstruction

RESUMO [in Portuguese]

A metodologia de conservação e restauração efetuada na maioria dos fosseis da gruta de Postes, Extremadura, é a mínima intervenção nos níveis de Plistoceno médio. Este nível está coberto por um espeleotema de 0,3 m com ossos completos aderidos, Unidade Estratigráfica Plistoceno 1.
Este trabalho descreve quatro tratamentos de restauração levados a cabo num dos fosseis deste nível desde seu descobrimento, para prevenir a sua deterioração e/ou total ou parcial perdida. Para remoção de osso foi necessário bater o espeleotema e fraturá-lo, danificando e quebrando o fóssil em fragmentos de pequeno tamanho. Os tratamentos consistiram em vendagem *in situ* e limpeza, consolidação e reconstrução no laboratório de investigação.
O fóssil foi recuperado e estabilizado e agora pode-se manipular. Os tratamentos permitiram identificar o osso como uma tíbia de *Ursus arctos*. Ademais o fóssil e o espeleotema foram analisados.

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INTRODUCTION

Archeo-paleontological remains are important because they provide essential information to understand an archeological site, and a certain time period. In many cases these fossil remains, must be treated in situ, given the fossil condition or the logistics of the site itself. The fossils found in limestone caves are often in contact with speleothems or calcic carbonate concretions. The fossil removal is difficult because the speleothem is harder than the bone. In order to extract them, it is usually necessary to use pneumatic hammers, screws and chisels that impart forces that can damage the materials. After an assessment of the fossil preservation, the integrity of the remains and stability must be ensured as much as possible until it is treated in the laboratory, with the purpose of carrying out scientific studies.

This work describes the required conservation-restoration treatments applied to a tibia inlayed in a speleothem from Postes Cave. The methodology accomplished follows the basic principles of the intervention methodology based in the modern discipline of conservation that appears in various official documents such as those from the International Council of Museums (ICOM-CC, 1984, 2008), European Confederation of Conservator-Restorers' Organisations (ECCO, 2003), and the American Institute for Conservation (AIC, 1994; López-Polín et al., 2008).

Postes Cave is part of the Natural Monument Fuentes de León Caves (DECRETO 124/2001; Badajoz, Spain) situated in the south of Extremadura, 7.5 km from the municipality of Fuentes de León. The caves are located in Cambrian grey and white limestone (between 500-540 Myr) and dolomite, with Quaternary grounds composed of decalcified clays (Figure 1; Díaz del Olmo et al., 1994; Algaba Suarez et al., 2000; Fernández-Amo and Rebollada, 2005; Durán, 2006; Fernández et al., 2007; Rebollada Casado et al., 2010).

The cave has an area of 180 m^2, divided in two stretches. The first one descends to a chasm filled in with clays. The first excavation was developed there within an area of 20 m^2 by 4.1 m of sedimentary potential, dated in the Holocene epoch. It is composed of Roman remains (Collado Giraldo, 2014; Collado Giraldo et al., 2015: 26) and a previous occupancy with an approximate chronology of 4140 +/-35 to 7780 ± 60 BP, dated by C^{14} with AMS and U/Th and anthracological results (Duque Espino, 2011; Collado Giraldo et al., 2015: 22-25). The second stretch finishes in two rooms with a different level separated by stalactite columns (Figure 2; Algaba Suarez et al., 2000).

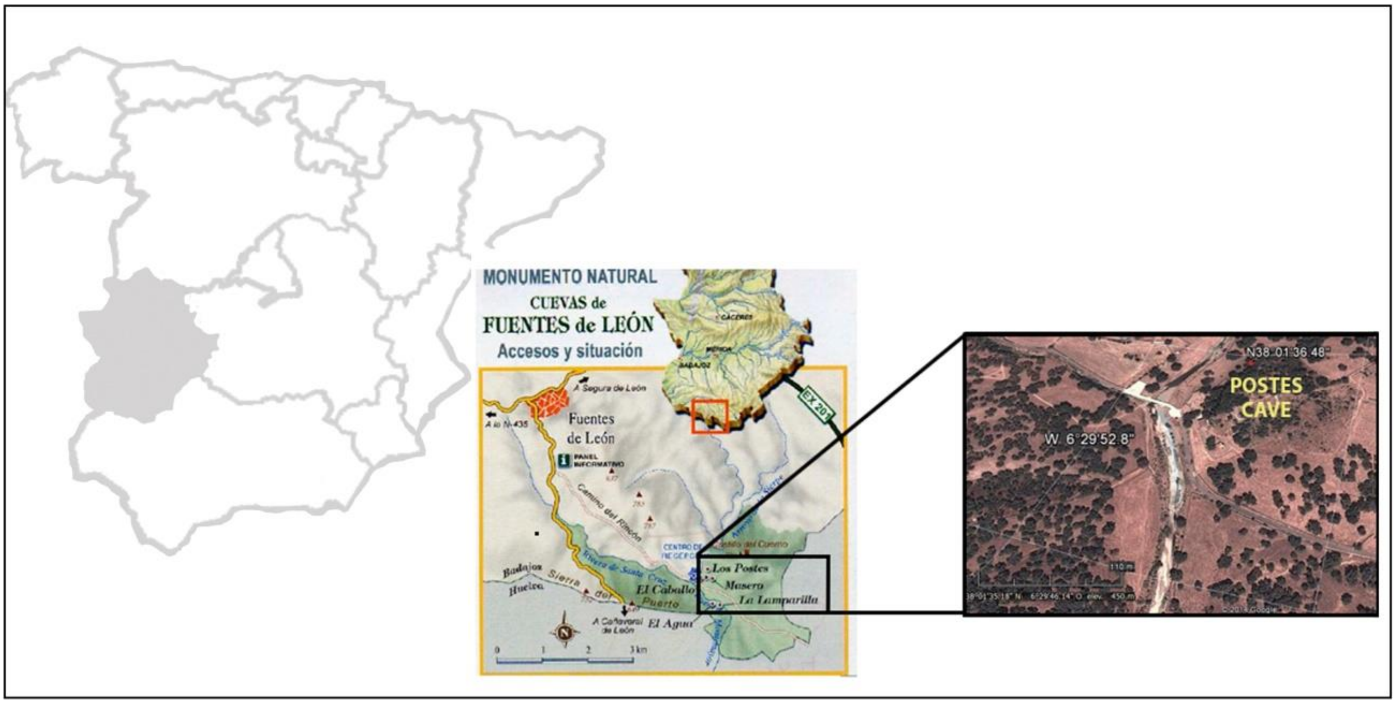

Figure 1 - Geographical location of Postes cave. From left to right, photos taken from "Programa conoce Extremadura: rutas por áreas protegidas de Extremadura (2012)" and Google Earth (2014).

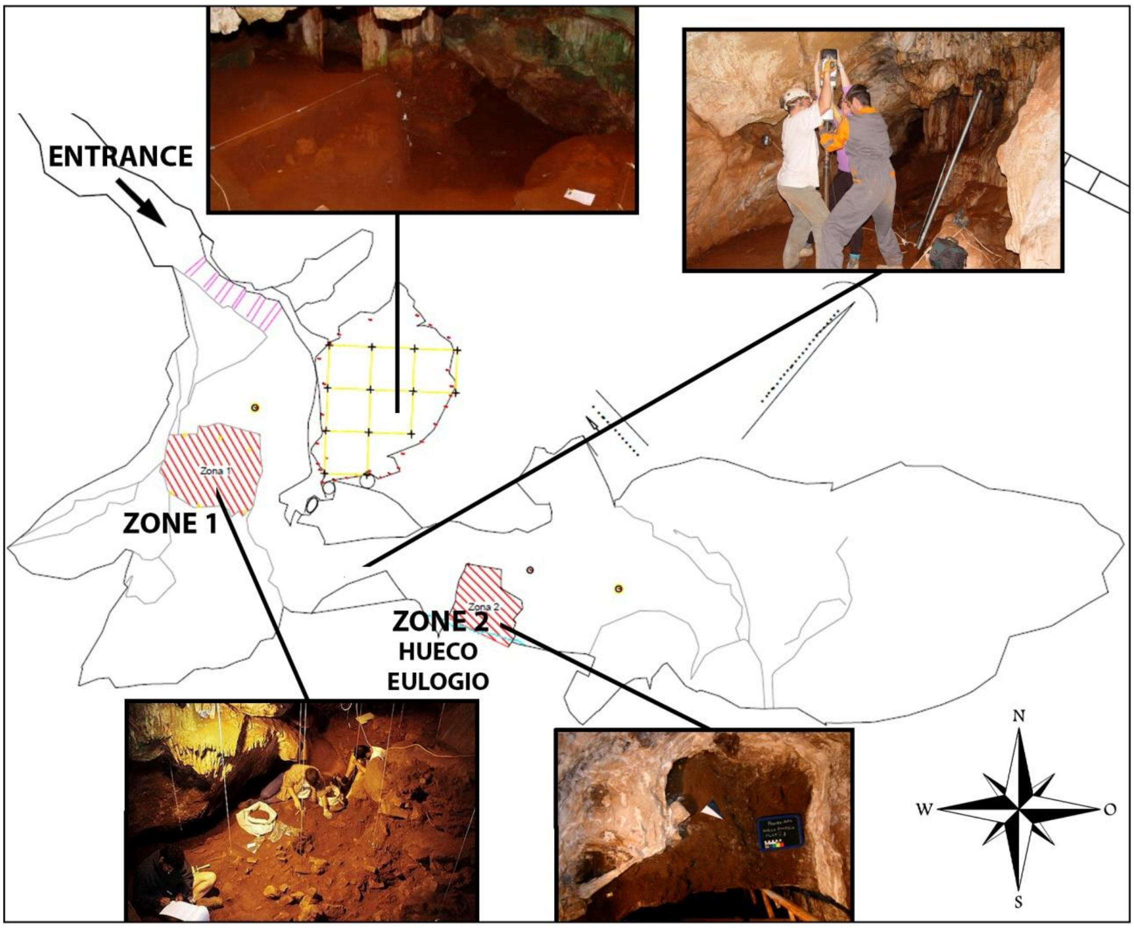

Figure 2 - Postes cave planimetry. Zone 1 indicates the first excavation area with Holocene layers. Zone 2 “Hueco Eulogio” indicates a posterior excavation, with Holocene and Pleistocene layers. Planimetry made by Samuel Pérez Romero under the direction of Hipólito Collado Giraldo. Photographs show the inside of the cave.

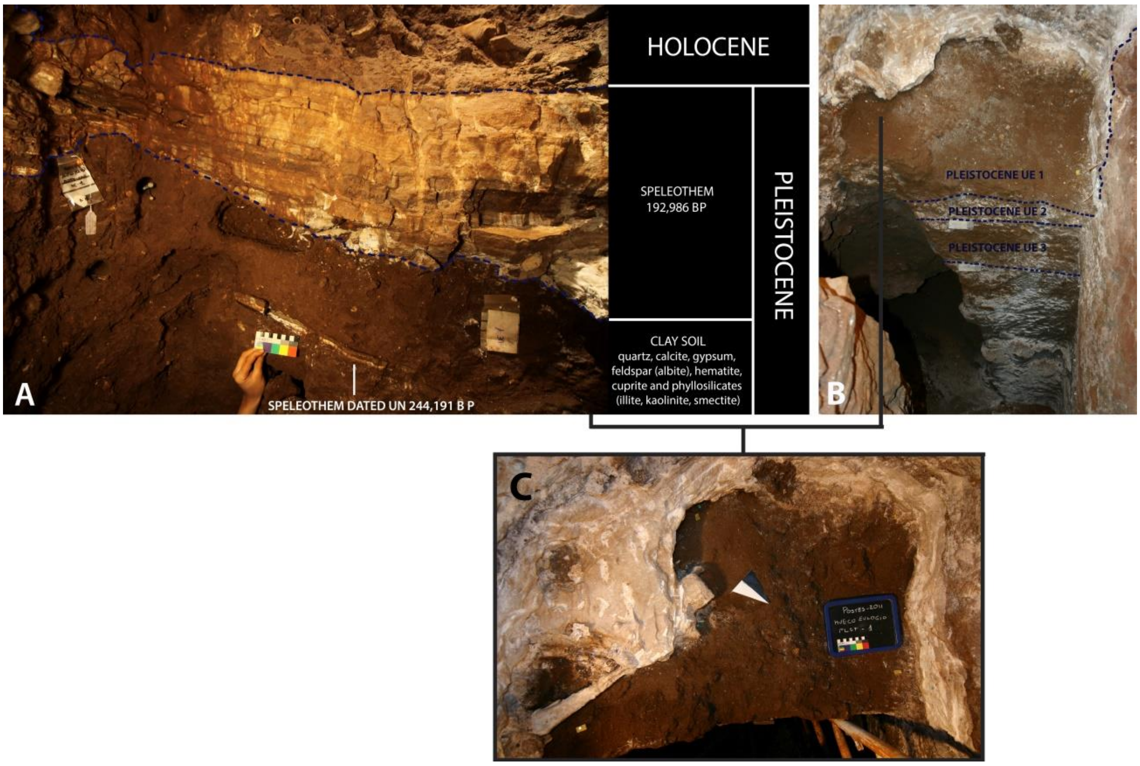

Figure 3 - A) Holocene and Pleistocene layers from Hueco Eulogio, eastern side. Pleistocene layer UE 1 is sealed by a speleothem dated to 192,986 +/-15,451-13,837 BP and a second one dated to 244,191+/-2261 BP. B) Pleistocene layers: Pleistocene UE 1- 7. Only the upper three layers containing remains so far are highlighted. C) Upper view of Pleistocene UE 1.

From 2009 to the present, a second excavation took place in an area of approximately 6 m^2 by 6 m of sedimentary potential, named "Hueco Eulogio". It contains Holocene and Pleistocene layers. Holocene layers are 450 mm high, and are composed of three basic stratigraphic units: UE 1 - UE 3 dated in Neolithic chronology (Duque Espino, 2011). Pleistocene layers are 4.7 m high, they are sealed by a calcitic crust dated to 192,986+/-15,451-13,837 BP and is approximately 0.3 m thick (Collado Giraldo et al., 2015: 26). It is composed of seven stratigraphic units (Pleistocene UE 1-7) with dates between 192,986 and 244,191+/-2261 BP obtained by U/Th (Figure 3).

The upper three layers, Pleistocene UE 1-3, contain black lithics made from silex, fossilized faunal remains, and a human phalanx (Collado Giraldo, 2014; Collado Giraldo et al., 2015: 26). Pleistocene UE 1 is composed of a speleothem where fossils are totally or partially adhered (Figure 4). The lower part of these fossils rest in a fill of lithified clay soil (Figure 5). It is composed of quartz, calcite, gypsum, feldspar (albite), hematite, cuprite and phyllosilicates (illite, kaolinite, smectite; Soutullo, 2013).

MATERIALS AND METHODS

The fossil treated is a complete left tibia belonging to and adult *Ursus arctos* (inventory number: Postes/12/Hueco Eulogio Pleistoceno/1/156) found in Zone 2 Hueco Eulogio, at the base of the speleothem and the roof of the clay soil from Pleistocene UE 1 layer, in the year 2011 (Figures 3 and 5). The removal of the speleothem was carried out by breaking it mechanically with a pneumatic hammer, screws and chisels. These actions broke the fossil in specific areas (Figure 5). Therefore, the conservation treatments and excavation had to be accomplished with close cooperation between archaeologists and conservators.

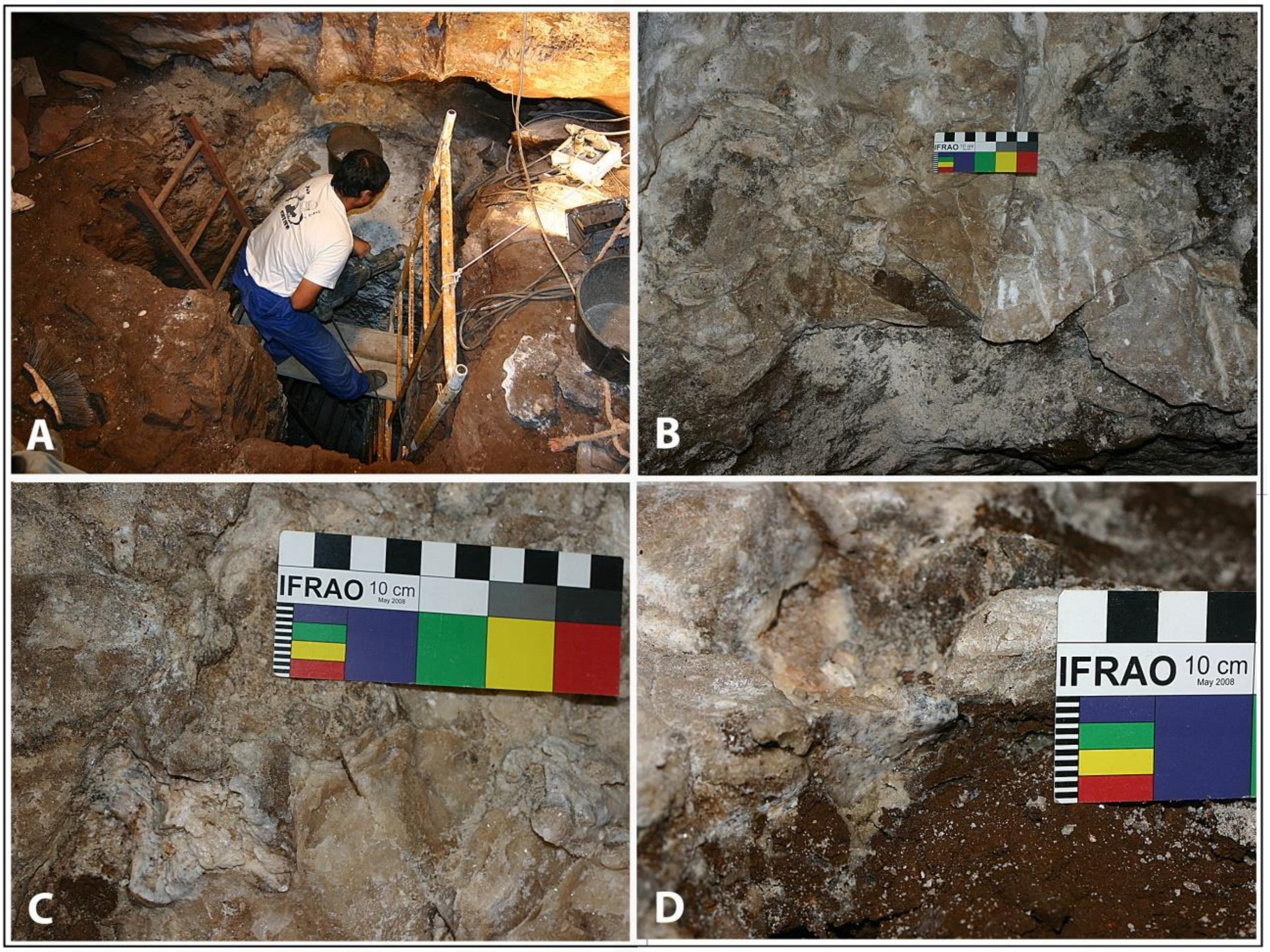

Figure 4 - Material adhered to the speleothem. A) First proceedings to break the speleothem by using a pneumatic hammer. B-D) Pleistocene UE 1 layer with fossils adhered to the speleothem.

The bone´s state of conservation was delicate, covered and adhered to the speleothem by both epiphyses, excluding the lower part that rested in the clay soil (Figures 3 and 5). The tibia is white, with black dots, possibly manganese. It presents fissures, fractures, grooves and dirt. The bone has a maximum length of 278.8 mm from the medial condyle to the medial malleolus, 76.9 mm high in the proximal epiphysis from the lateral condyle to the medial condyle, 44.4 mm high in the distal epiphysis and 25.6 mm high in the diaphysis (Figure 5).

As a conservation factor, environmental agents are kept stable in cave sites so that fossils do not become deteriorated when they are exposed during excavation work and conservation-restoration treatments (Ortega et al., 2009). This fact avoided further major deterioration during their extraction.

Conservation-restoration treatments were accomplished in two phases. The first one was in situ and consisted in consolidation and the application of bandage. The second phase was in the restoration laboratory and consisted of the removal of the bandages, further consolidation, cleaning, reconstruction and

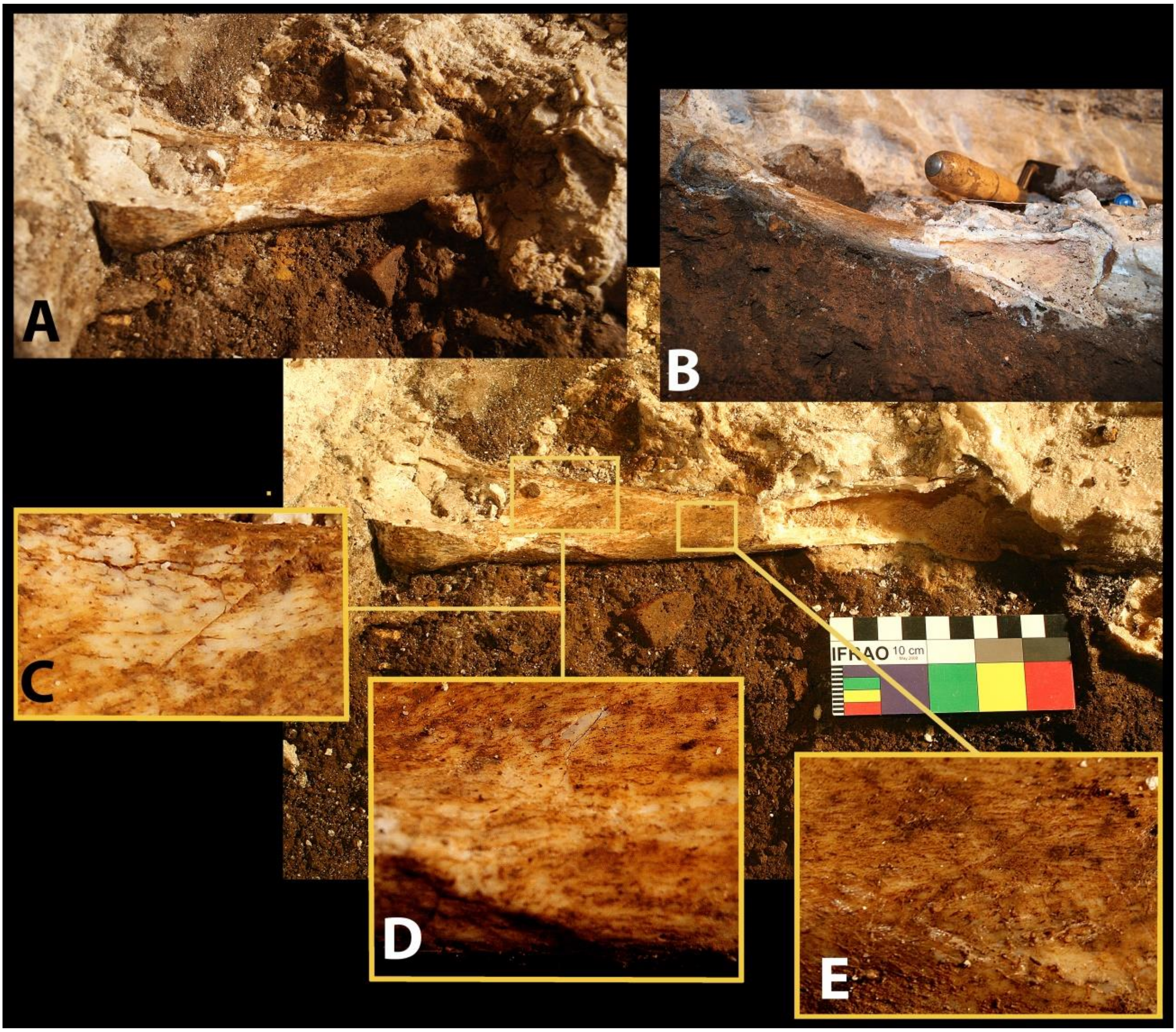

Figure 5 - A-B) Bone´s state of conservation during the archaeological work. The fossil is still adhered to the speleothem in its epiphyses. C) The top of the diaphysis has been cleared revealing some new and older fractures D) fissures and E) grooves (Image credit José Enrique Capilla).

application of a protective layer. Bone deterioration was evaluated, while different treatments were accomplished. They were carried out simultaneously preventing the disintegration of the small fragments. Prior to the interventions, an evaluation of the state of conservation and/or deterioration of the bone was made, in order to act accordingly.

For consolidations, adhesions and re-constructions we used the acrylic resin Paraloid B-72® in varying proportions diluted in CH_3COCH_3 (acetone; Storch, 1983; Koob, 1986; Johnson, 1994; Kres and Lovell, 1995; Down et al., 1996; Davidson and Alderson, 2009; Davidson and Brown, 2012; López-Polín, 2012). For the removal of the bandage and cleaning we required the same solvent, CH_3COCH_3, which was used to dissolve the Paraloid B-72.

In situ treatments

During the removal of the fossil, the speleothem was fractured with a hammer and chisel, leaving the diaphysis surface of the bone isolated. During this work the tibia broke into pieces, losing part of the bone in both epiphyses which were adhered to the speleothem (Figure 5).

Damages and possible consequences of the forces and pressures imparted in the fossil during the extraction were analyzed together with the archaeologists. We made a bandage to completely envelop and reinforce the bone against continuous hits. Before this, we applied a layer of consolidant over the surface with 5% Paraloid B-72 diluted in acetone. The bandage was carried out with gauze strip bandages (about 5-10 cm long) intertwined, attached with 15% Paraloid B-72 diluted in acetone applied by brush (Figure 6).

The fossil was pulled out in one piece. For that to happen, we had to hit the speleothem and fracture it. After applying pressures on the bone in diverse directions we observed a fracture and displacement in the diaphysis medial area (Figure 7). The fossil was packed and transferred to the laboratory.

Figure 6 - Bandage in situ. Application of medium- sized strip bandages over the whole surface and reinforcement of the epiphysis with larger strips (Image credit José Enrique Capilla).

Figure 7 - A) Fossil after extraction. B) Detail of fracture and displacement in the medial diaphysis region.

Treatments in restoration laboratory

The bone state of conservation was evaluated in the research laboratory. The fossil consists of a gauzed main fragment and 20 isolated fragments, most of them from the epiphysis without gauzed, and speleothem remains. The bone presents a displacement in the diaphysis medial area and various fractures (Figure 7).

In the laboratory, we removed the bandage, cleaned, consolidated, and glued the fragments, reconstructed and laid out a protective layer. Some of these treatments were carried out simultaneously to prevent the disintegration of small fragments.

Removal of the bandage. Bandage removal consisted in the impregnation of the gauzed surface with acetone applied with brushed-on solvent until several layers could be separated with the help of tweezers. We started in the diaphysis medial area due to the bone´s distortion in that region. We used scissors to cut the strips, separating the fossil in two parts (Figure 9). At the same time a thick layer of 5% Paraloid B-72 diluted in acetone was applied between the fragments to prevent their detachment. Treatments continued in both parts separately (Figures 8 and 9).

The bone conservation state after the bandage treatments was unstable. The fossil was fractured in small fragments, these fractures were new, several fragments were displaced and some of them presented laminations. There is loss of bone in specific areas. In the caudal view of the proximal tibia we could see loss of the lateral condyle, not seeing the facet for articulation with the fibula (Figure 10). The lateral view of the distal tibia possibly presents loss of bone in the cochlea. There are remains of calcitic concretions in the central and cranial intercondylar area. The lateral view of the proximal tibia presents a displacement of the fragments inside, and the surface was filled in with sediment and consolidant. Finally, the entire fossil presented superficial dirt with remains of sediment, consolidant and threads (Figure 10).

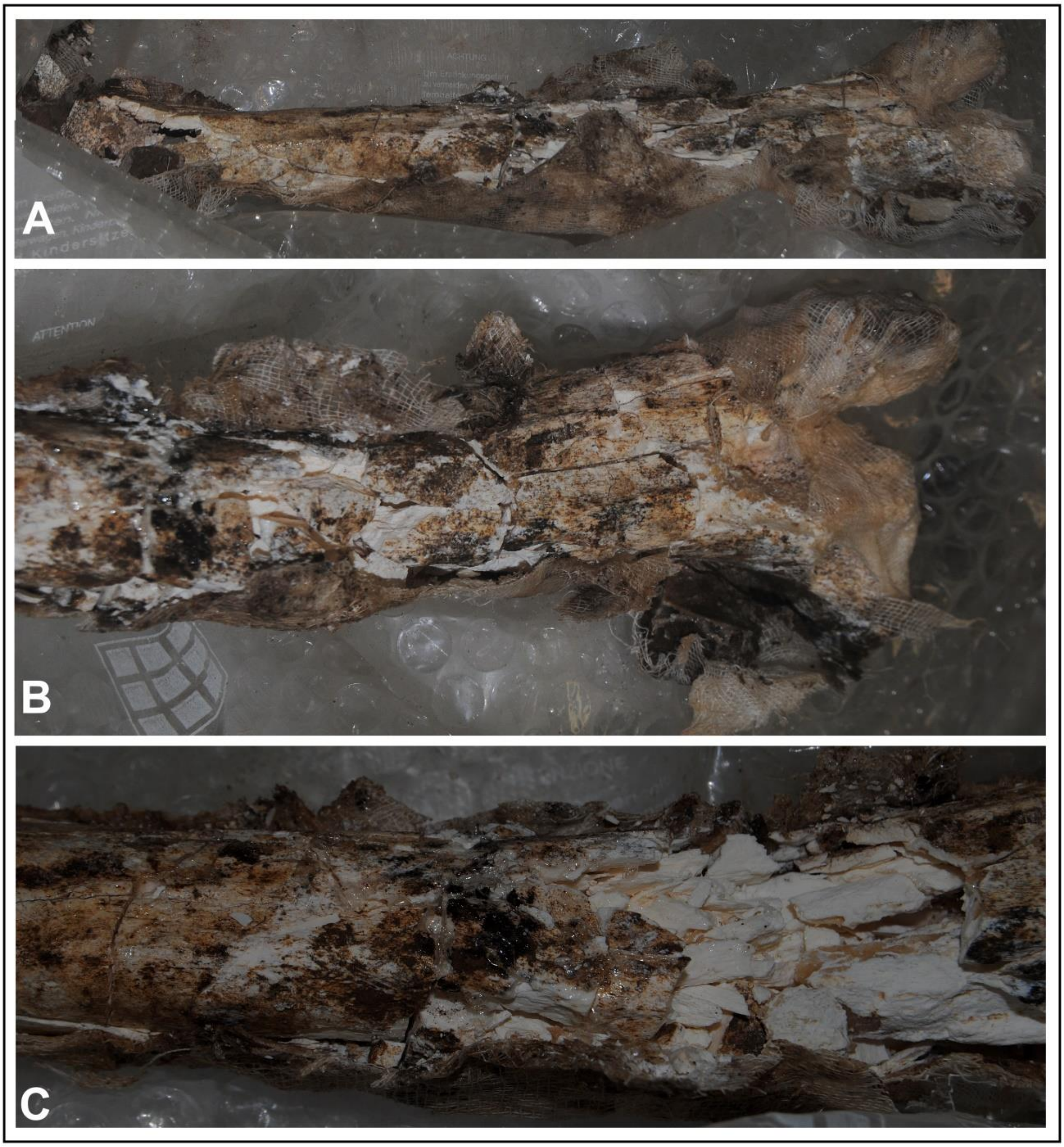

Figure 8 - A-B) Removal of the bandage in the caudal view. It Presents loss of bone and fractures with small fragments. C) Detail of the loss of bone in the diaphysis.

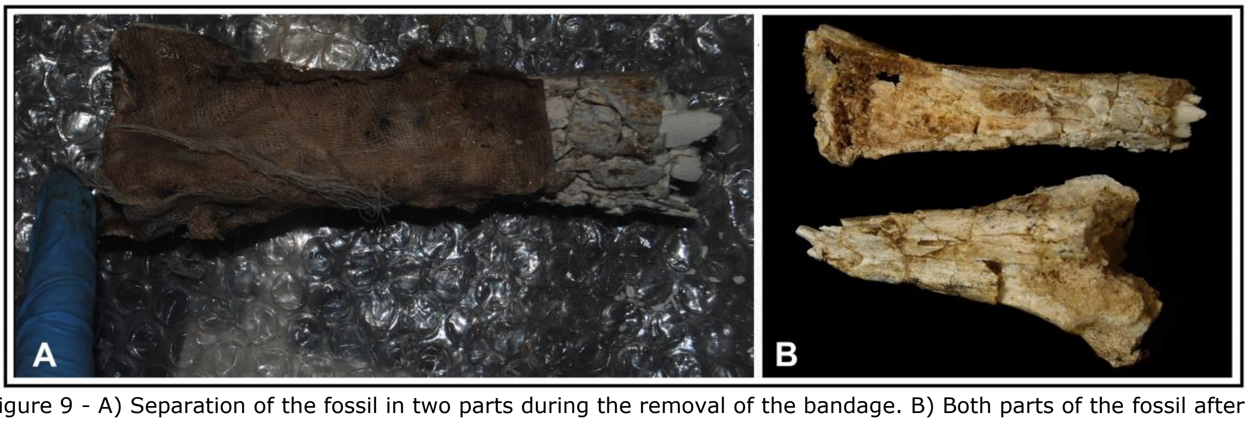

Figure 9 - A) Separation of the fossil in two parts during the removal of the bandage. B) Both parts of the fossil after the removal of the bandage.

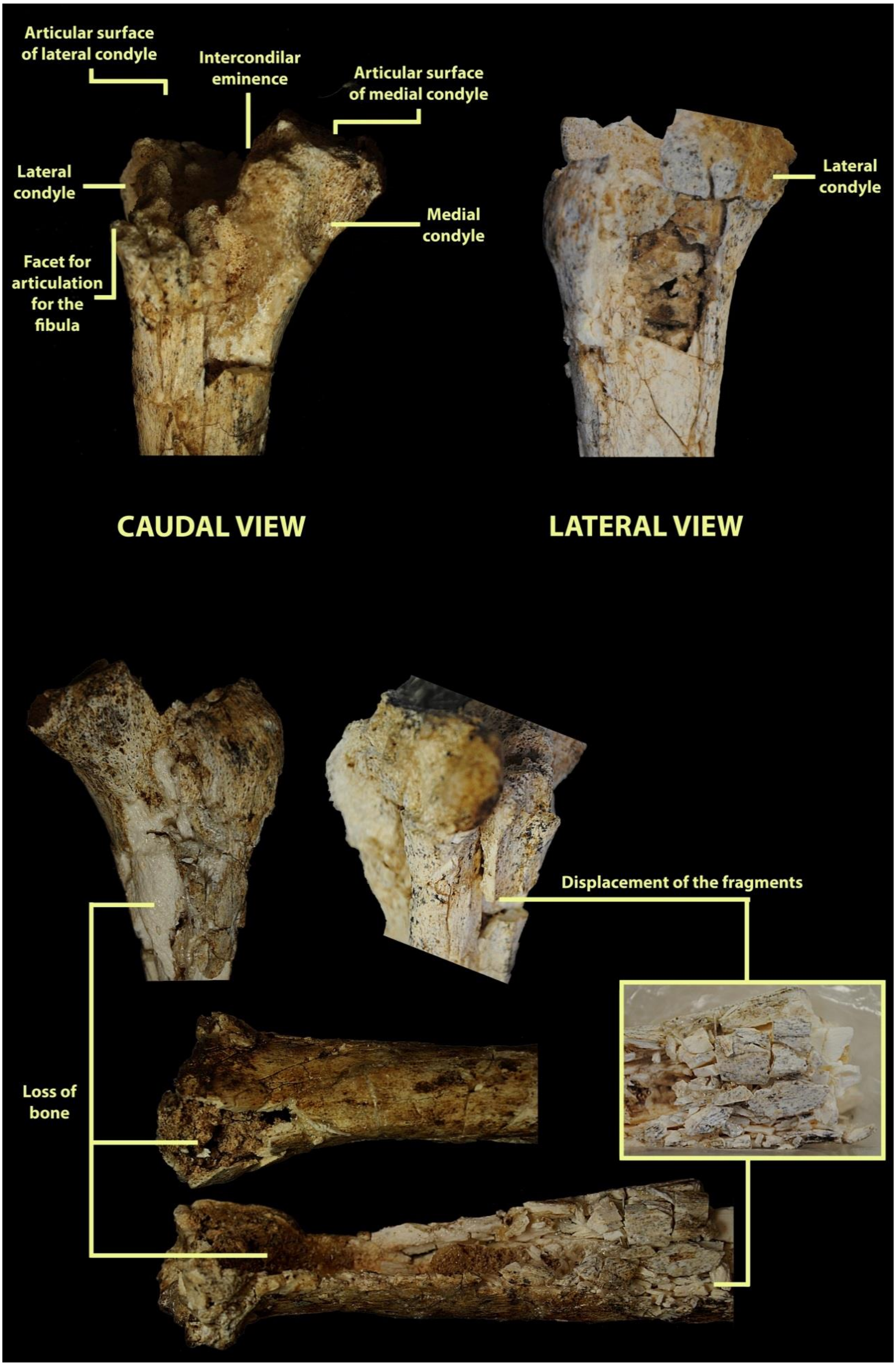

Figure 10 - Diagnosis of the fossil before the cleaning and reconstruction.

Cleaning and reconstruction. Cleaning and reconstruction were achieved simultaneously in both parts of the fossil. Cleaning treatments consisted in the removal of the dirt, consolidant and threads. We impregnated the surface with solvent using a brush and cotton swabs, which were able to sweep along the dirt until it was eliminated (Figures 10 and 11).
In some areas we had to clean, consolidate and fill some gaps with adhesive. At the same time some fragments were relocated. In other areas a sketch was made to make the posterior separation of the fragments easier prior to the cleaning and reconstruction (Figures 11-17). We explain the treatments made in specific areas of the fossil, proximal and distal parts and the joint of both, below.

After the cleaning we observed that the fragments from the surface between the diaphysis and the proximal epiphysis had been displaced inside, which had caused an obvious deformation. Its separation was difficult, so we decided to separate the lateral condyle to simplify the task. Previously we made a sketch, giving a number to each fragment and to aid future reconstruction (Figure 12 A-F). After cleaning treatments that favored a good fit, we decided to apply adhesive in all of the fragments and adhere them at the same time (Figure 12 G).

The same procedure was achieved in the diaphysis and distal epiphysis that presented a displacement of some of their fragments (Figure 13).

In the distal fragment we proceeded with the distal diaphysis reconstruction. This part was the most vulnerable during the excavation work. Therefore, it presented new fractures made up of small and displaced fragments, loss of bone in specific areas and adhered sediment that did not allow them to fit together. A sketch of the area was made, followed by separation of the fragments, cleaning them individually and joining them together, while we corrected the displacements. The millimeter-size fragments from the interior of the bone that didn´t allow good fitting were removed (Figure 14). A big fragment from the diaphysis was adhered, and a chopstick was placed to avoid movements (Figure 15).

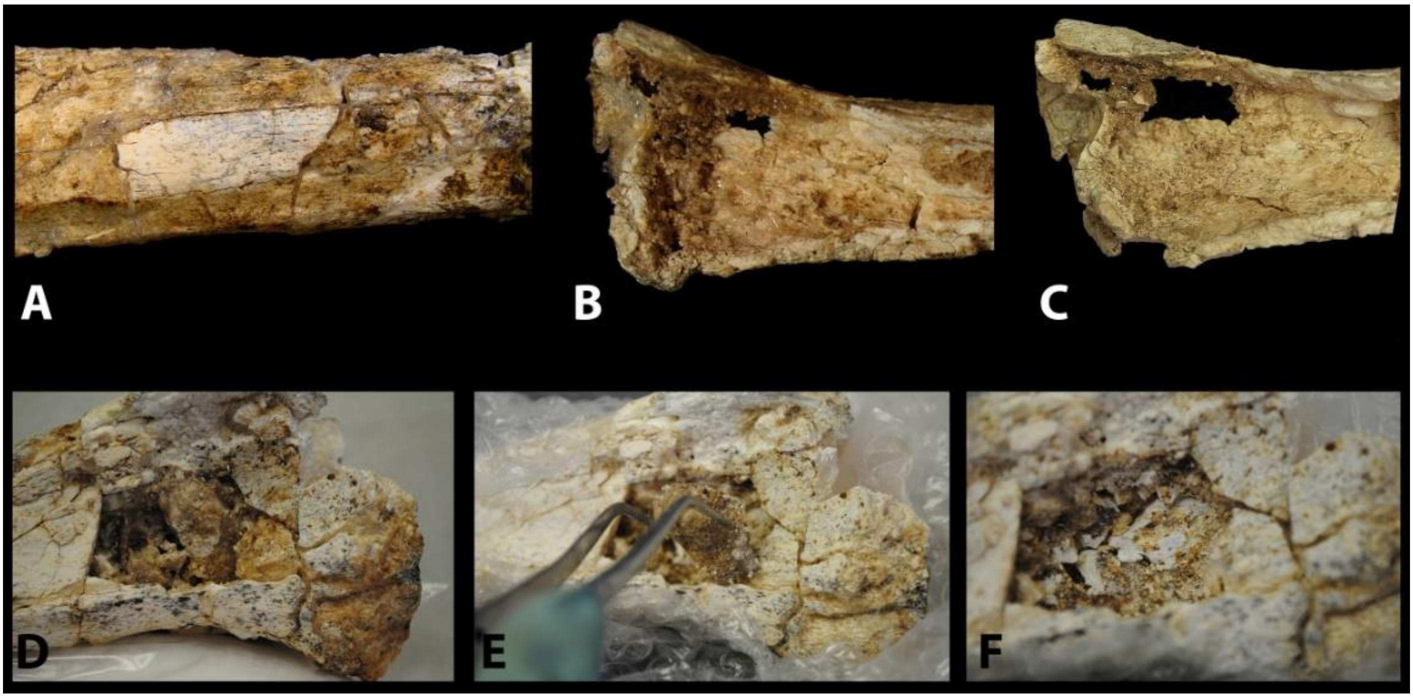

Figure 11 - During cleaning treatments. A) Superficial cleaning. B-C) Cleaning of the distal epiphysis. D-F) Removal of the sediment from the proximal epiphysis, cranial view.

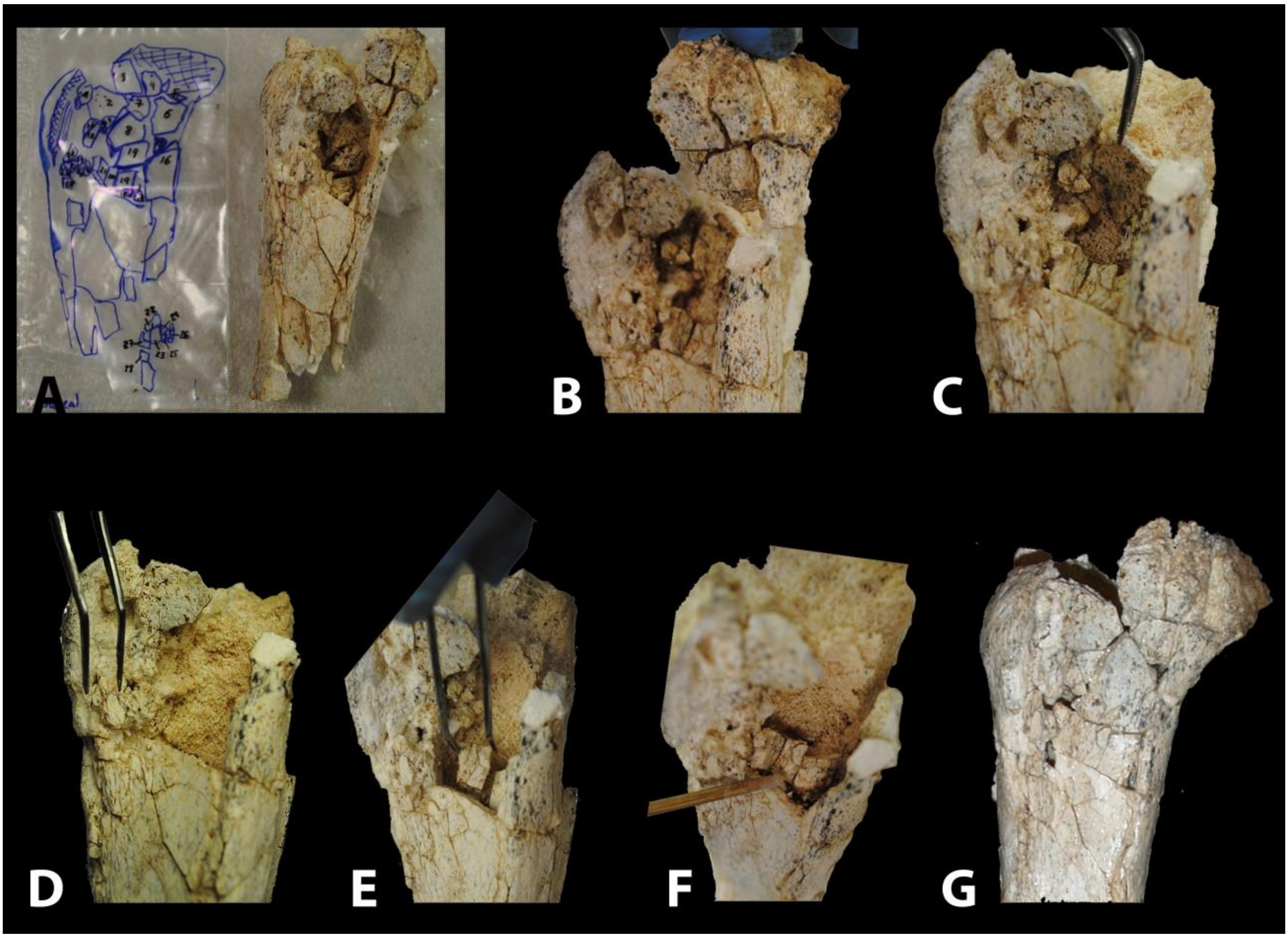

Figure 12 - Reconstruction of the proximal epiphysis. Lateral view: A) Sketch with the fragments numbered. B) Separation of lateral condyle. C-F) Cleaning and removal of the displaced fragments. G) Epiphysis view after restoration treatments.

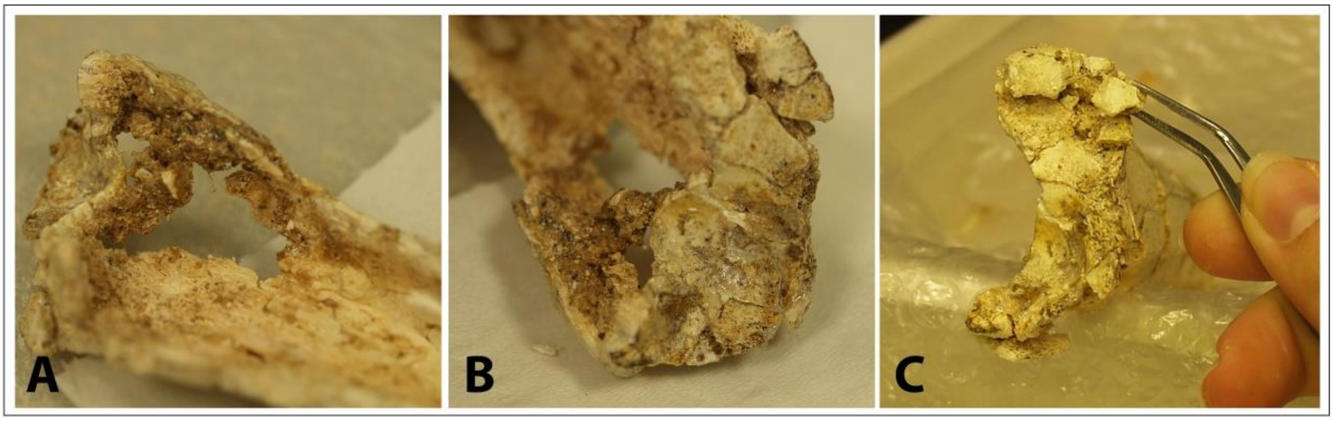

Figure 13 - Reconstruction of the distal epiphysis: A-B) Distal epiphysis before the cleaning and reconstruction. C) Cleaning and relocation of the fragments from distal epiphysis.

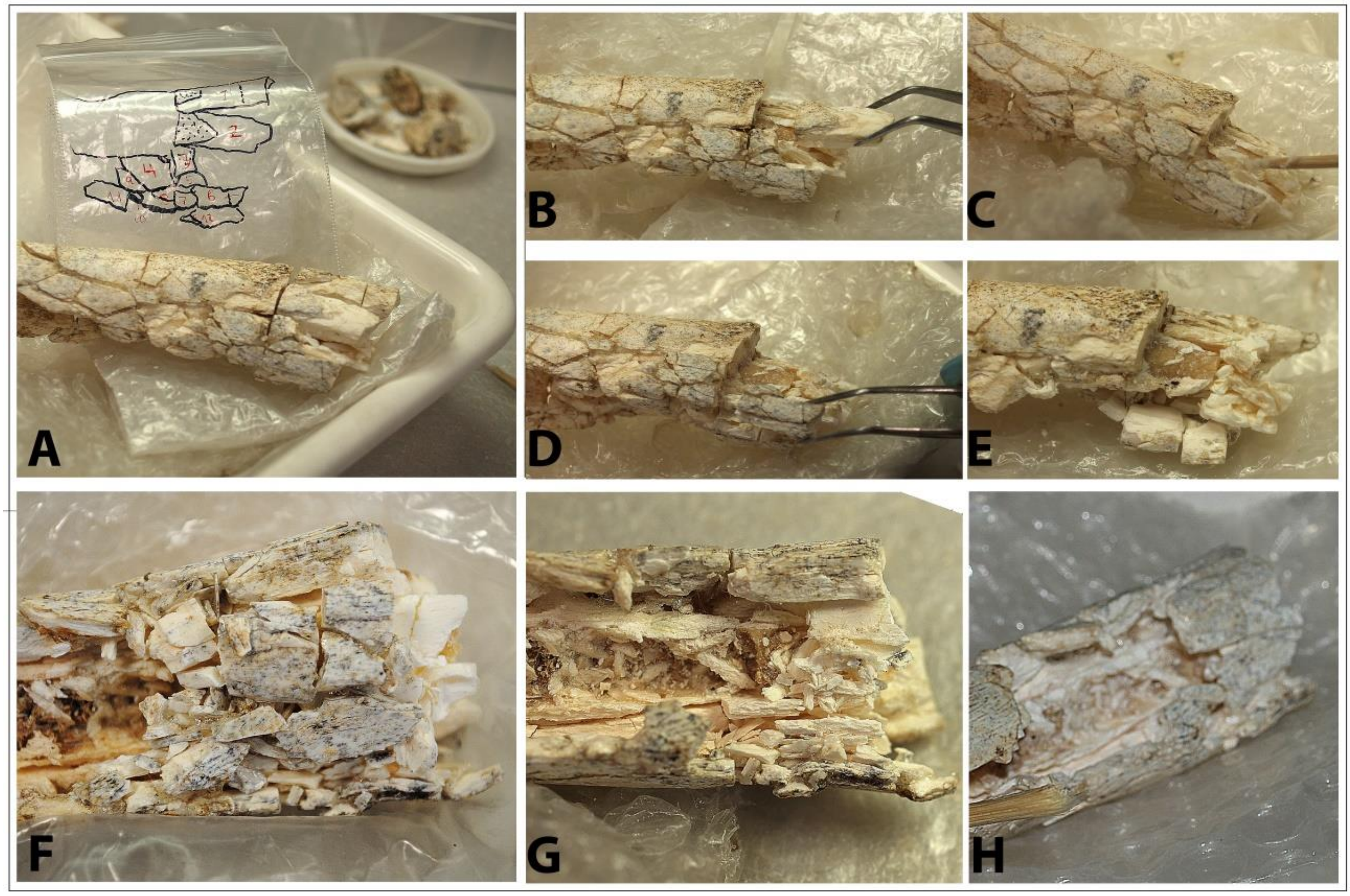

Figure 14 - Cleaning and reconstruction of the distal diaphysis: A) Sketch of the numbered fragments. B-G) Cleaning and separation of displaced fragments for the posterior right position. H) Diaphysis view after the reconstruction.

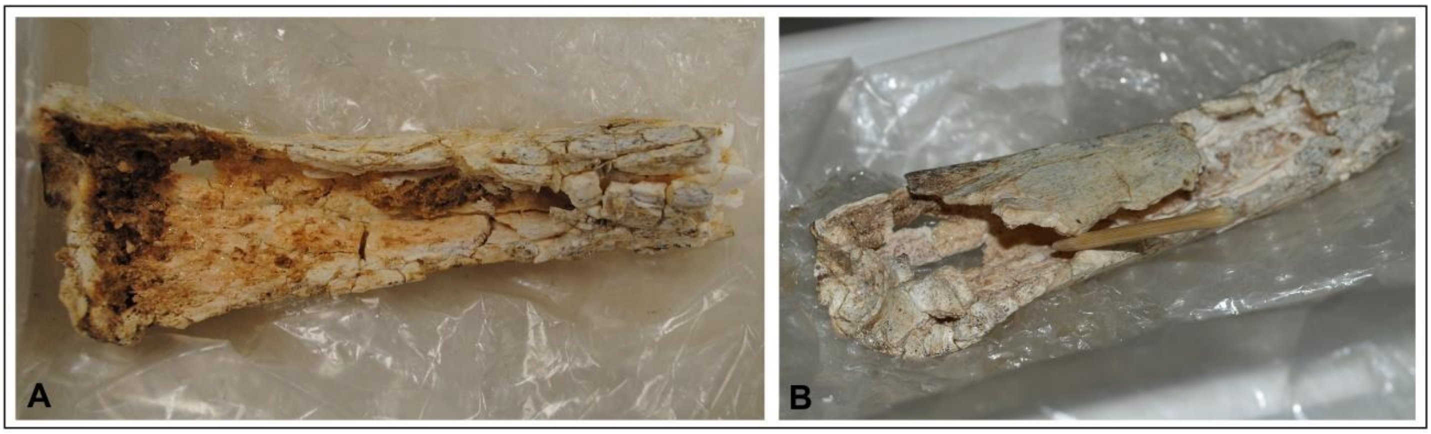

Figure 15 - A) Incomplete distal epiphysis. B) Additional support used to adhere a big fragment from the diaphysis.

The same approach was taken in the medial diaphysis, and new fittings were found for isolated fragments. While the reconstruction of this area was achieved, we were checking the good fit of both halves of the diaphysis. To prevent movements, the fragments were held with a clear plastic sheet and an elastic band (Figure 16).

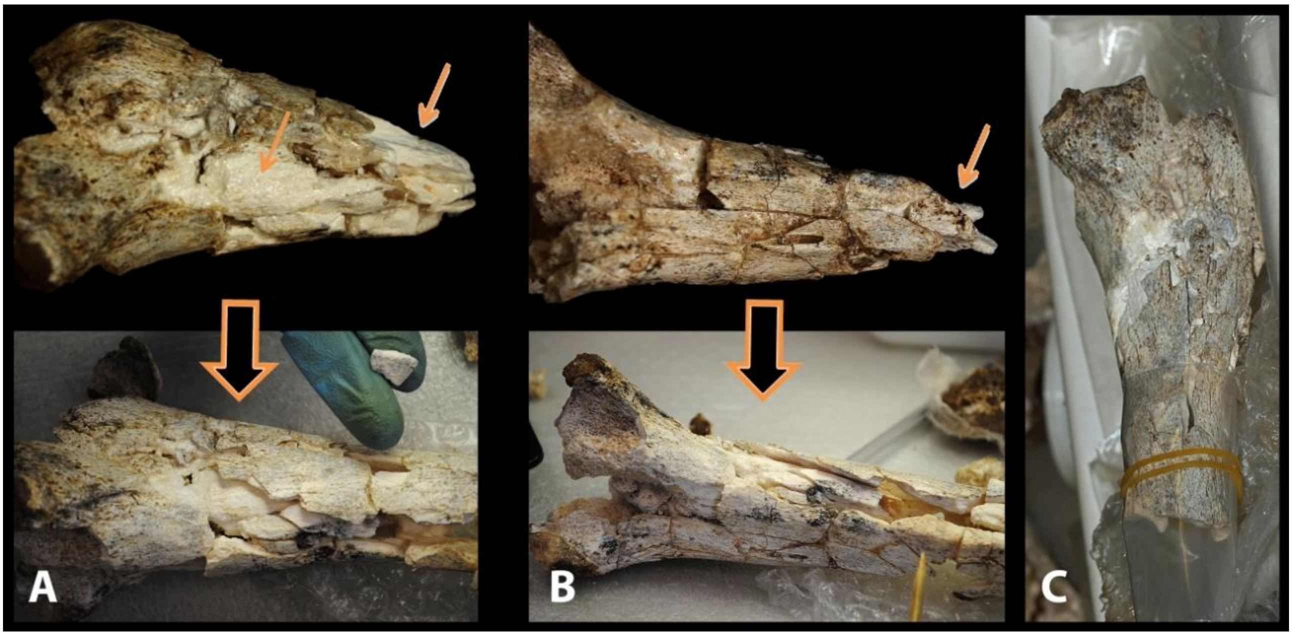

Figure 16 - A-B) Adhesion of some fragments form the proximal diaphysis, lost during the excavation work. Those areas that present loss of bone are marked with arrows. C) Fastening of the fragments adhered in the diaphysis with a clear plastic sheet and an elastic band.

Figure 17 - Final result of the left tibia. Left to right: medial, cranial, lateral, caudal views.

Figure 18 - Storage of the fossil after finish restoration treatments.

Reconstruction treatments were finished by joining together both distal and proximal parts (Figure 17). Their surfaces were protected with a thin and homogeneous layer of consolidant (3% Paraloid B-72 diluted in acetone).

Preventive conservation measures were taken to protect the fossil in its housing, with an expanded polystyrene package able to minimize movements. It was stored in a box to block the entrance of dust (Figure 18). It is recommended to keep it in constant environmental parameters, a temperature of 18º to 21°C with a fluctuation of 1,5° and a relative humidity of 45 - 55% out of direct sunlight.

RESULTS

The intervention in the tibia was carried out in two phases; the first one was achieved in situ and consisted in the protection of the fossil with a bandage that prevented the deterioration and made its extraction from a calcitic matrix easier. Fossils located within these speleothems often get fractured or even lost. In this case, the fossil broke into numerous small fragments and suffered displacement. The bandage managed to maintain a unified structure during the excavation work.

The second phase was accomplished in the laboratory and consisted in the removal of the bandage, which served to evaluate the damage and continue with the cleaning and reconstruction treatments simultaneously.

These treatments required the ability to diagnose bone alterations and solve the problems in both the extraction procedures, and in the conservation treatments. This also requires the knowledge of conservation techniques and products plus knowledge of the bone material itself (López-Polín et al., 2008).

After conservation-restoration treatments the bone presents more optimal state of conservation. Moreover, this work has allowed us to recover the whole anatomy of the fossil, it can now be studied by hand, and suitable for accomplishing paleontological studies. It has been taxonomically determined to be an *Ursus arctos* left tibia.

DISCUSSION AND CONCLUSIONS

Conservation treatments achieved in the tibia here described were necessary since the removal of the fossil in situ. Stabilization of the bone was greatly affected by the stalagmitic crust that covered it. This is a common characteristic within karst sites. In such a situation we found pertinent that excavation and conservation staff work together to be able to analyze the state of conservation precisely and prevent the potential deterioration during excavation. In addition, the skills in the methodology and the knowledge of the bones morphology is essential when they are inlayed in calcitic matrix.

We hope that this study will provide a valuable contribution in the field of conservation, and will serve not only as a standardized set of protocols relevant to the protection of paleontological material, but also to bring to attention the importance of the conservation process in the preservation of the fossil specimens, from the moment of excavation, to their deposition in a research center (Ortega et al., 2009).

In any case, the intervention was accomplished having in mind the bone stability and its needs. Deterioration was prevented and a whole view of the fossil was obtained. It is available for scientific studies that will provide a better understanding of these Pleistocene periods.

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REFERENCES CITED

AIC. 1994. Code of Ethics and Guidelines for Practice. The American Institute for Conservation of Historic & Artistic Works, Washington, DC, USA, 10 pp.

Algaba Suarez, M., H. Collado Giraldo, and J. M. Fernandez Valdez. 2000. Cavidades En Extremadura. British Archaeological Reports, Oxford, UK, 74 pp.

Collado Giraldo, H. 2014. La mano que escondía la cueva. Aventura de La Historia 190:78–81.

Collado Giraldo, H., J. R. Bello Rodrigo, I. M. Domínguez García, L. F. Nobre da Silva, L. Rodríguez Dorado, J. M. Torrado Cárdeno, M. Villalba de Alvarado, J. González Márquez, A. C. Domínguez García, E. García, E. Garrido Fernández, J. E. Capilla Nicolás, E. Oyola Macías, M. Giles Domínguez, C. Castaños Ceballos, R. Montero, S. Pérez Romero, and D. M. Duque Espino. 2015. "ORÍGENES": un proyecto de investigación del monumento natural "Cuevas de Fuentes de León" y su influencia en la economía local. Revista de estudios extremeños 71:13–36.

Davidson, A., and S. Alderson. 2009. An introduction to solution and reaction adhesives for fossil preparation. Methods In Fossil Preparation: Proceedings of the First Annual Fossil Preparation and Collections Symposium 53–62.

Davidson, A., and G. W. Brown. 2012. ParaloidTM B-72: practical tips for the vertebrate fossil preparatory. Collection Forum 26:99–119.

Díaz del Olmo, F., R. Baena, and G. Álvarez. 1994. Karst y paleokarst de Sierra Morena (sector Ossa-Morena, Hespérico meridional). Espeleotemas 4:15–24.

Down, J. L., M. A. MacDonald, J. Tetreault, and R. Scott Williams. 1996. Pruebas de adhesivos en el Canadian Conservation Institute-una evaluación de una selección de adhesivos acrílicos y de acetato de polivinilo. Cuadernos Sobre Conservación 41:12–21.

Duque Espino, D. M. 2011. Anthracology in the Caves of Fuentes de León (Badajoz, Extremadura, Spain): notes for the characterization of the plant environment of the neolithic communities and Roman period of the SW of the Iberian Peninsula. SAGVNTVM Extra 11:175–176.

Durán, J. 2006. Guía de Las Cuevas Turísticas de España. Instituto Geológico y Minero de España, Madrid, Spain, 108 pp.

ECCO. 2003. E.C.C.O. Professional Guidelines (II). European Confederation of Conservator-Restorers' Organisations A.I.S.B.L., Brussels, Belgium, 4 pp.

Fernández, F. J., D. Carvajal, R. Merino, and E. Rebollada. 2007. Datos para el aprovechamiento turístico de las Cuevas de Fuentes de León; pp. 57–66 in J. J. Durán, P. A. Robledo, and J. Vázquez (eds.), Cuevas turísticas, aportación al desarrollo sostenible. (Serie Hidrogeología, Aguas subterráneas). Instituto Geológico y Minero de España, Madrid, Spain.

Fernández-Amo, F. J., and E. Rebollada. 2005. Punto de interés geológico Cuevas de Fuentes de León; pp. 131–134 in P. Muñoz Barco and E. Martínez Flores (eds.), Patrimonio Geológico de Extremadura. Consejería de Agricultura y Medio Ambiente, Badajoz, Spain.

ICOM-CC. 1984. The conservator-restorer: a definition of the profession. 7th Triennal Conference.

ICOM-CC. 2008. Terminology to characterize the conservation of tangible cultural heritage. 15th Triennal Conference 1–2.

Johnson, J. S. 1994. Consolidation of archaeological bone: a conservation perspective. Journal of Field Archaeology 21:221–233.

Koob, S. P. 1986. The use of Paraloid B-72 as an adhesive: its application for archaeological ceramics and other materials. Studies in Conservation 31:7–14.

Kres, L. A., and N. C. Lovell. 1995. A comparison of consolidants for archaeological bone. Journal of Field Archaeology 22:508–515.

López-Polín, L. 2012. Possible interferences of some conservation treatments with subsequent studies on fossil bones: A conservator's overview. Quaternary International 275:120–127.

López-Polín, L., A. Ollé, I. Cáceres, E. Carbonell, and J. M. Bermúdez de Castro. 2008. Pleistocene human remains and conservation treatments: the case of a mandible from Atapuerca (Spain). Journal of Human Evolution 54:539–545.

Ortega, M. C., A. Gracia, J. M. Carretero, I. Martínez, R. Quam, and J. L. Arsuaga. 2009. Restauration d'un fémur fossile humain du site de la Sima de los Huesos (Atapuerca, Espagne). L'Anthropologie 113:233–244.

Rebollada Casado, E., F. J. Fernández-Amo, G. Álvarez García, and H. Collado Giraldo. 2010. Historia de las exploraciones de las cuevas turísticas de Fuentes de León (Badajoz); pp. 575–586 in J. J. Durán and F. Carrasco (eds.), Cuevas: Patrimonio, Naturaleza, Cultura y Turismo. Asociación de Cuevas Turísticas Españolas, Madrid, Spain.

Soutullo, B. 2013. Informe Técnico de Sedimentología. Laboratorio de Difracción de Rayos X. Universidad Complutense de Madrid, Madrid, Spain.

Storch, P. S. 1983. Field and laboratory methods for handling osseous materials. Conservation Notes 1–4.

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IN SITU CONSERVATION STRATEGIES AT THE PLEISTOCENE SITES OF PINILLA DEL VALLE, MADRID (SPAIN)

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ABSTRACT

The aim of this study is to describe the conservation and restoration procedures applied to the Pleistocene archaeological sites of Camino Cave, Navalmaíllo Rock Shelter and Buena Pinta Cave of Pinilla del Valle, Madrid (Spain). Clear-cut and timely decisions must be made when retrieving fossils and the close collaboration of a multidisciplinary team is the key to success. Early diagnosis is made in situ to determine the state of conservation and decay. A balance is sought between what the bones need, the available resources and the scientific data requirements of each site.

The principle of minimum intervention is followed throughout the entire process. Sub-fossils that were not successfully extracted were sent to the laboratory where a new diagnosis was performed. Previously collected on-site data provide helpful information for performing treatments that ensure the material's structural stability. The last step is careful packing of the bones pending further study.

Keywords: conservation; archaeological; preservation; sub-fossil; multidisciplinary approach; bones

RESUMO [in Portuguese]

O objetivo deste estudo é a descrição dos procedimentos de conservação e restauro aplicados aos sítios arqueológicos Pleistocenos de Cueva del Camino, Abrigo de Navalmaíllo e Cueva de Buena Pinta em Pinilla del Valle, Madrid (Espanha). No momento de recuperação dos fósseis é necessário tomar decisões efetivas de forma rápida e a colaboração comuma equipa multidisciplinar é a chave para o sucesso. É realizado um diagnóstico in situ para determinar o estado de conservação e deterioração. Procura-se umequilíbrio entre as necessidades dos materiais, os recursos disponíveis e as exigências científicas de cada sítio.

O princípio da mínima intervenção é aplicado ao longo de todo o processo. Os fósseis que não passaram com sucesso a fase de extraçãos ão enviados para o laboratorio onde é realizado um novo diagnóstico. Os dados recolhidos previamente no sítio fornecem informação útil na realização de tratamentos que asseguram a estabilidade estrutural do material. O último passo é o acondicionamento cuidado do material pendente de estudos futuros.

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INTRODUCTION

Archeological and/or paleontological remains from the Pleistocene provide invaluable information that aids us in comprehending past occurrences at the sites. This information allows us to increase our understanding of hominid behavior and their relationship with their environment. Many of the materials, particularly bone remains, must be treated during the excavations (in situ and at the field laboratory). In these interventions, assessment by different members of the team, such as paleontologists, archeologists and geologists, is essential for the performance of diverse studies.

In order to develop a correct work methodology, establishing a rapid and precise appraisal of the fossils' state of conservation and/or decay is important, starting from the very moment they are found. In some cases, they must be immediately protected to avoid their decay. These urgent treatments must not damage the integrity of the bone material and therefore the products that are applied must be compatible with the material, reversible and must not interfere with future analyses. Furthermore, the procedures that are performed must be appropriately documented, so that all the professionals involved have access to this information. Throughout the entire process, the basic principles of conservation must be followed, in accordance with official conservation requirements (i.e., ICOM-CC, 1984, 2008; AIC, 1994; ECCO, 2003), and adapted to the specific issues pertaining to the archeological and/or paleontological sites of Pinilla del Valle.

GEOGRAPHIC AND GEOLOGICAL FRAMEWORK

The archeological and/or paleontological sites at Pinilla de Valle are located at an altitude of approximately 1100 m at the Calvero de la Higuera, which forms part of the central sector of the Valle Alto (High Valley) of the Lozoya River. This is located in the Sierra de Guadarrama, a mountain range in the Spanish Central System (Pérez-González et al., 2010).
The first site to be discovered was Camino Cave, which was excavated during the 1980s and 1990s by Prof. Dr. Alférez (Alférez et al., 1982, 1985; Alférez and Roldán Garrido 1992). In 2002, a new phase of studies initiated, which is continued today by the interdisciplinary team directed by J. L. Arsuaga, E. Baquedano and A. Pérez-González. In the following years, new sites were discovered and their excavations were initiated: the Navalmaíllo Rock Shelter, Buena Pinta Cave and Des-Cubierta Cave.

These sites are a reference point in the study of the Upper Pleistocene ecosystems on the Iberian Peninsula. Camino Cave was a hyena den, Navalmaíllo Rock Shelter served as a Neanderthal campsite, and Buena Pinta cave hosted sporadic settlements of hominids, as well as a hyena den. Des-Cubierta Cave was the last site to be discovered, and it is currently being studied (Figures 1, 2; Baquedano et al., 2010, 2011; Arsuaga et al., 2011, 2012; Márquez et al., 2013, in press; Laplana et al., 2016; Arriaza et al., in press).

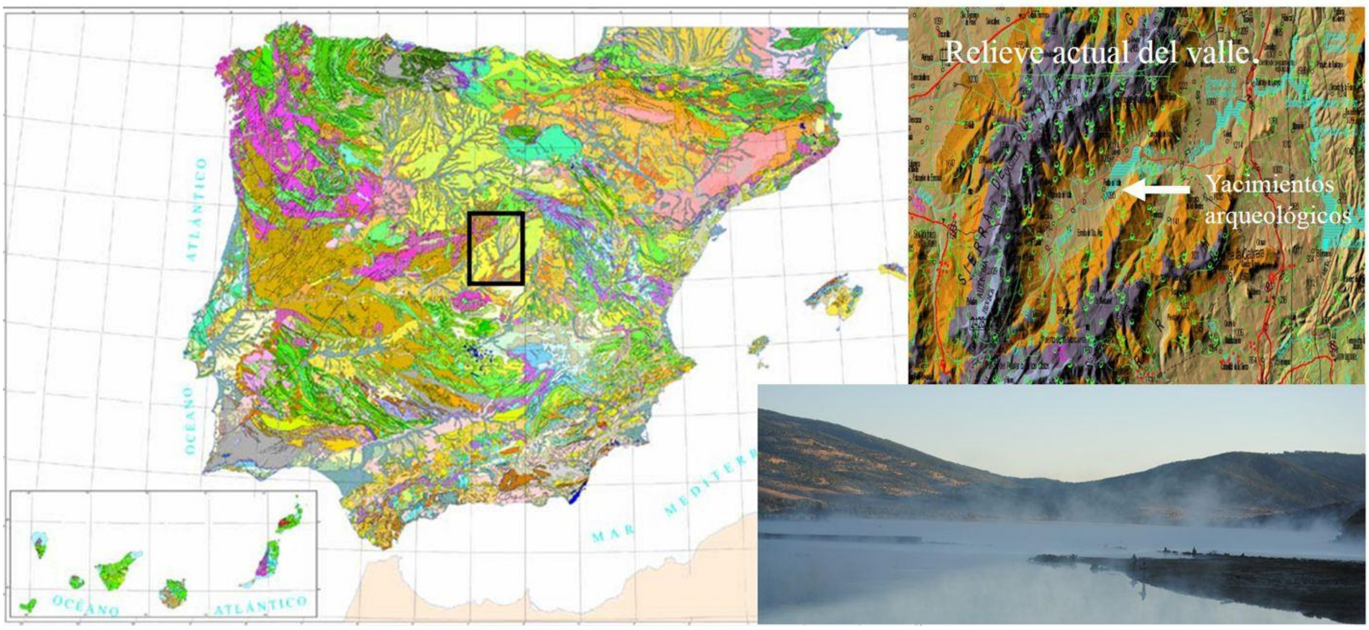


Figure 1 - Morphogeographic location of the Pinilla del Valle sites in the High Lozoya Valley (Sierra de Guadarrama).

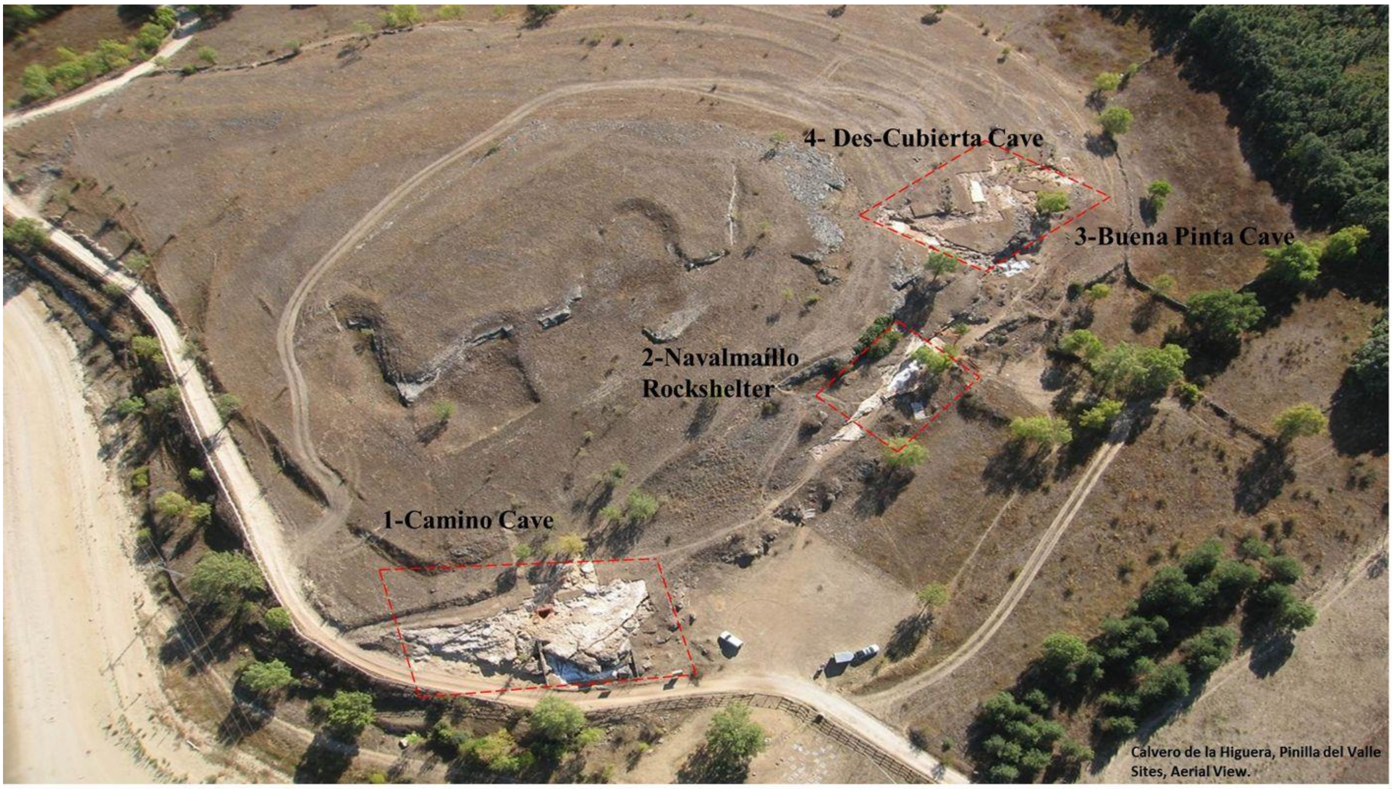
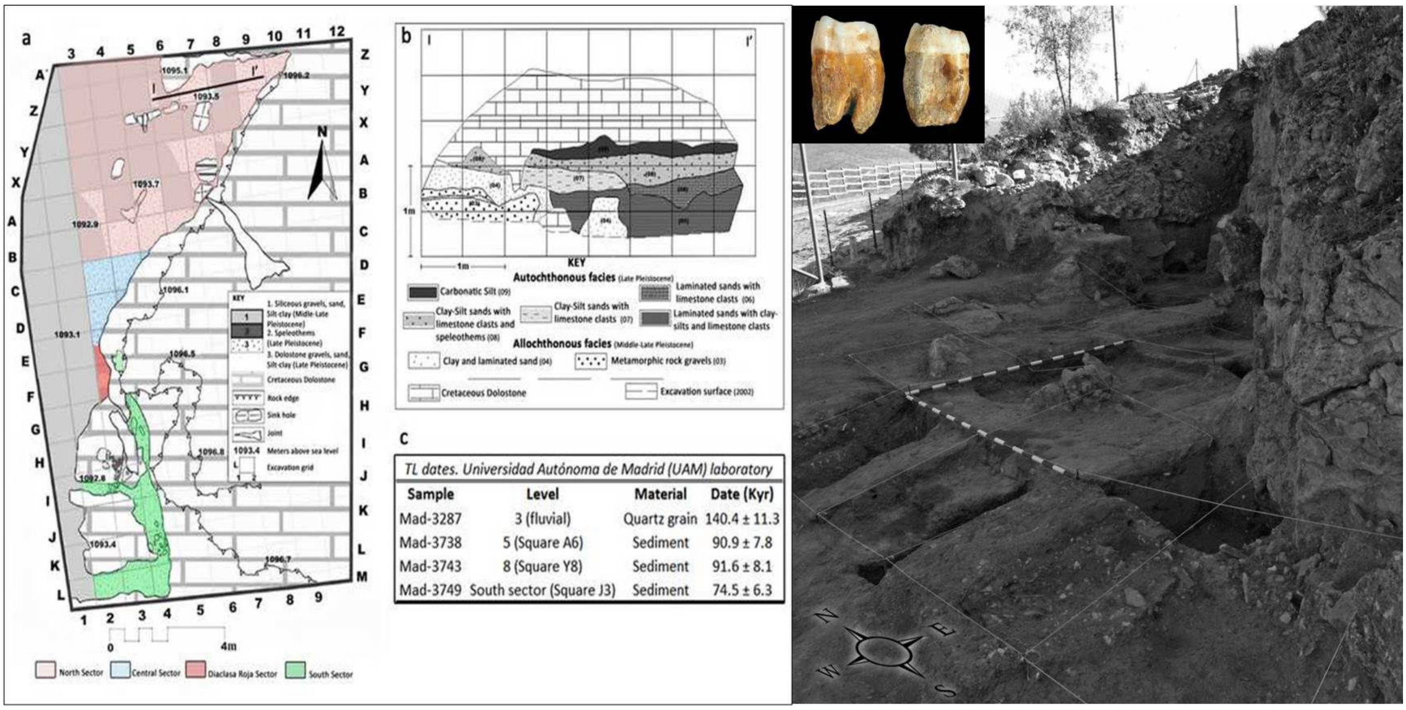


Figure 2 - Aerial view of the Pinilla del Valle sites: 1) Camino Cave, 2) Navalmaíllo Rock Shelter, 3) Buena Pinta Cave and 4) Des-Cubierta Cave.



Sample	Level	Material	Date (Kyr)
Mad-3287	3 (fluvial)	Quartz grain	140.4 ± 11.3
Mad-3738	5 (Square A6)	Sediment	90.9 ± 7.8
Mad-3743	8 (Square Y8)	Sediment	91.6 ± 8.1
Mad-3749	South sector (Square J3)	Sediment	74.5 ± 6.3

Figure 3 - Left: Site map showing the four sections of the excavated areas and the location of the samples for thermoluminescence dating (A) and the stratigraphic sectors mentioned above (modified from Pérez-González et al., 2010; Arsuaga et al., 2012). Right: the Cueva del Camino site and the *Homo neanderthalensis* molars (photo by Pinilla del Valle Research Team, PVRT).

The Camino Cave site is part of the Calvero de la Higuera archaeological complex located in the Upper Valley of the Lozoya River. Geologically, the upper valley of the Lozoya river lies within the Shale-Grauváquico Complex of the Central Iberian Zone. The Calvero de la Higuera sites are associated with cavities that evolved from the Late Cretaceous carbonate rocks. The resulting relief has been dissected by the Lontanar and Valmaíllo streams (Arsuaga et al., 2010).

The Camino Cave site is located 130 m north of the Navalmaíllo Shelter, 6-7 m above the Valmaíllo and Lontanar valleys. The original karst has suffered a high grade of erosion that hinders recognition of the original morphology (Alférez et al., 1982, 1985; Alférez and Roldán Garrido 1992; Arsuaga et al., 2012). The Cueva del Camino site is formed by four sectors (Figure 3): North, Central, Diaclasa Roja and South sectors. The stratigraphic sequence of the karstic sedimentary fill includes levels 3 to 9, thermoluminescence analysis has been performed on level 5 dated to 90961 ± 7881 ka. This level concentrates the major part of the paleontological finds (Pérez-González et al., 2010).

The Navalmaíllo Rock Shelter site was discovered in 2002 by the current research team, located 8 meters above the Navalmaíllo Stream Valley. The shelter, one of the cavities in the Calvero de la Higuera slope, occupies an area of some 300-400 m² (Baquedano et al., 2010, 2011, 2014; Huguet Pàmies et al., 2010; Arsuaga et al., 2011; Márquez et al., 2013).

The stratigraphic sequence includes 8 levels: A to F, plus Alpha and Beta (Figure 4). Hearth structures and burned bones with cut marks have been found in the fertile levels. The high degree of fragmentation and distribution of the bone remains provides a clear evidence of human activity, pointing out that the shelter was occupied by Neanderthal groups. Level F, which has provided the largest amount of the archaeological remains, has been dated to 71685 ± 5082 and 77230 ± 6016 ka by thermoluminescence (Baquedano et al., 2010, 2011, 2014; Huguet Pàmies et al., 2010; Arsuaga et al., 2011; Márquez et al., 2013; Arriaza et al., in press).

The Buena Pinta Cave was discovered in 2003 as a result of the archaeological surveys carried out by the Pinilla del Valle Research Team. The phreatic cavity, with a 1.5 elliptical cross-section, is 10 meters long and opens to the N-NE through the Cretaceous carbonate rocks. Five levels have been found, showing a stratigraphic continuity both at the external chamber and the gallery (Figure 5; Pérez-González et al., 2010; Arsuaga et al., 2011; Baquedano et al., 2011; 2014; Laplana et al., 2016). Levels 2 to 5 are rich in late Pleistocene macro- and microvertebrate remains (Laplana et al., 2016). Level 3 has been dated to 63451 ± 5509 ka by thermoluminescence (Pérez-González et al., 2010).

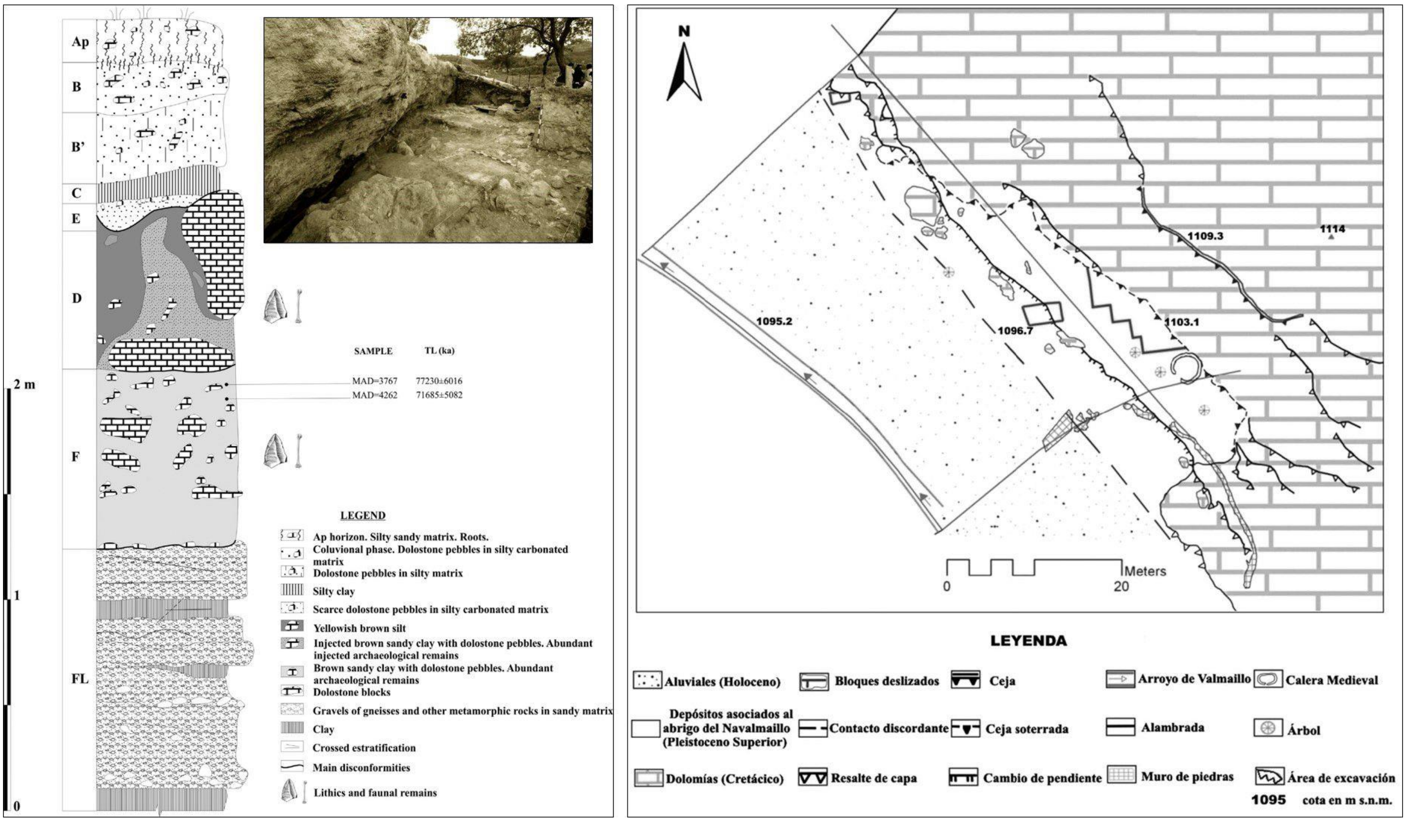


Figure 4 – Right: General view and stratigraphic (Arriaza et al., in press). Left: Plan of the Navalmaíllo Rock Shelter (Pérez-González et al., 2010).

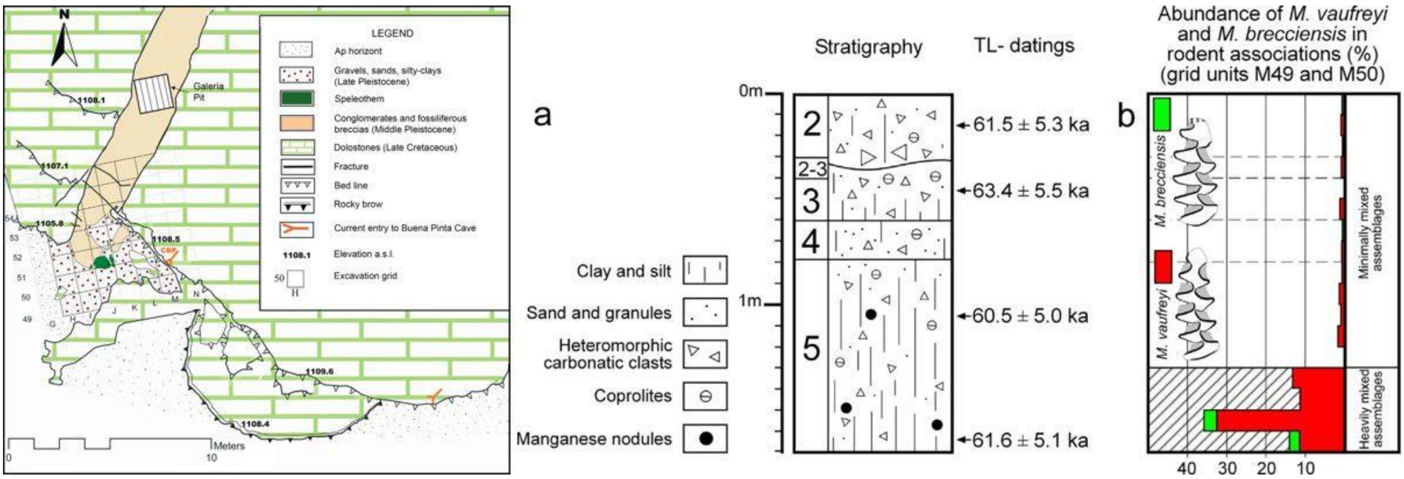


Figure 5 - Left: Plan scheme of the Buena Pinta Cave site, Modified from (Pérez-González et al., 2010). Right Stratigraphy of the external chamber of the Buena Pinta Cave, indicating the provenance of the sediment samples dated by thermoluminescence, and the ages obtained (Dating and Radiochemistry Laboratory, UAM; Laplana et al., 2016).

THE MATERIAL AND ITS STATE OF CONSERVATION

The sub-fossils presented in this article have been recovered in excavation campaigns that took place between 2006 and 2014. They belong to Camino Cave, Navalmaíllo Rock Shelter, and the Buena Pinta Cave. Knowing how the space was used at the different sites is important, because their past occupation directly impacted the type of objects found and was reflected in their state of preservation and/or decay.

During treatment, our main priority is to stabilize the fossils, but the scientific needs of each site have also to be taken into account. In a site occupied by carnivores, such as Camino Cave and partially Buena Pinta Cave, the finds included exclusively bone material and coprolites. Conservation aims to preserve the taphonomic information, which is why the fossils should all remain in situ as a whole, allowing for a complete overview of bone positioning.

In a site that had been occupied by humans, such as Navalmaíllo Rock Shelter, bone and lithic materials both occur, with the latter occurring in greater proportion. The sub-fossils are fragmentary and there is a scarcity of complete bones and teeth. Here, the scientific needs are archeological, taxonomic and taphonomic, and interventions are minimal due to the bones' good state of preservation.

Another important factor includes changes in moisture in the depositional environment during sedimentation and before excavation; if the sub-fossils are found in environments with the aforementioned changes, decay is caused by cracking: the bones crack and even fracture in a mosaic pattern.

Bone material from **Camino Cave** included in this study was recovered between 2006 and 2009. This assemblage is composed of fragments, some of them quite complete, e.g. the cranial-dental bones, the long bones, and a limited representation of small bones. Decay, due to fissuration or fracturation in the long bones, was longitudinal and transversal (separating bones in two). The main alterations we found were superficial and associated with diagenetic modifications: concretion crust produced by carbonates, crenulated edges and polished surfaces, root marks, cracking and exfoliation, along with marks of carnivore activity (> 70%), such as punctures, perforations, pitting, scoring and fractures (Figure 6; Table 1; Arsuaga et al., 2012).

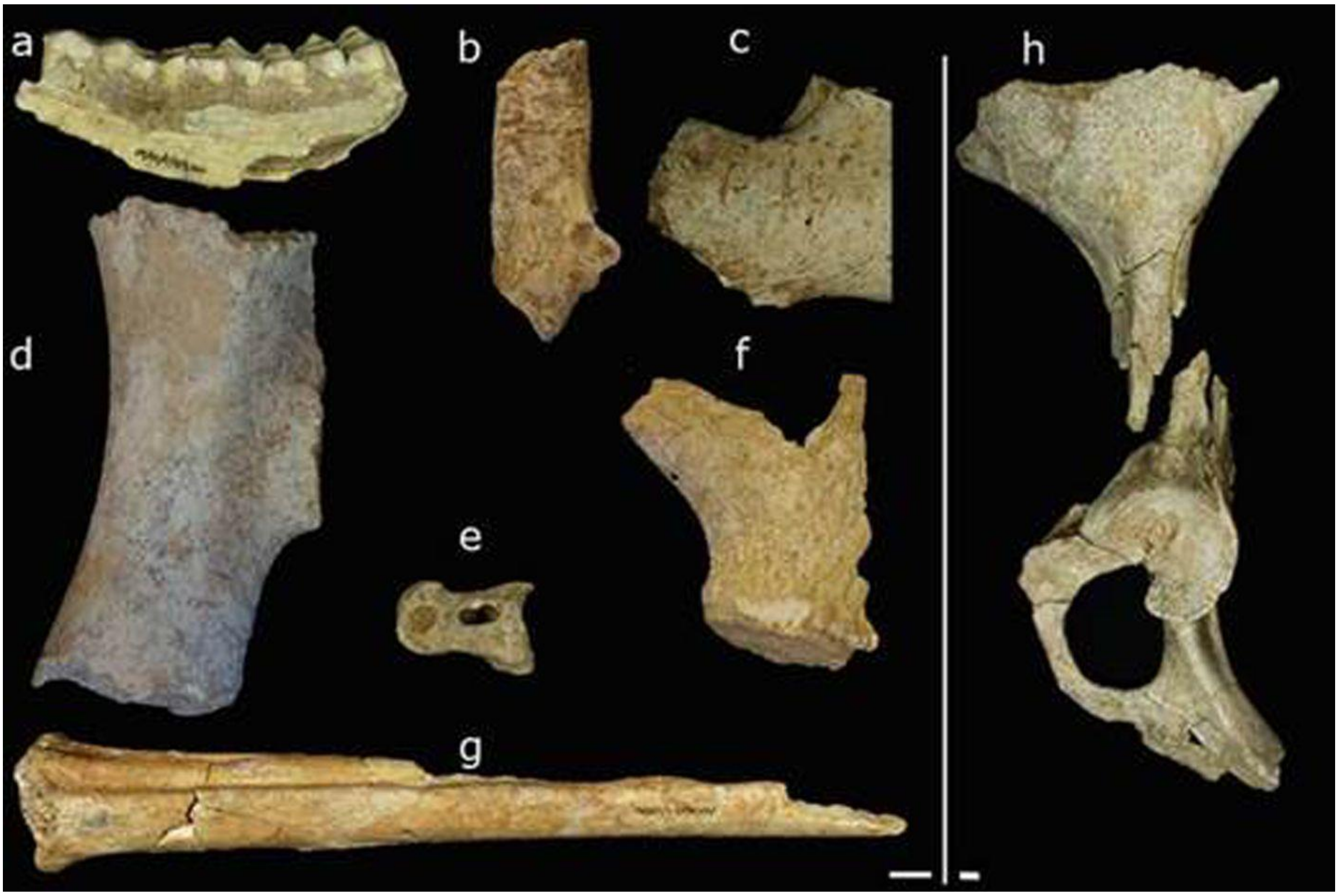


Figure 6 - Carnivore activity marks on bone remains from Camino Cave. A) Left mandible of *Dama dama* showing crenulated edges; B) Right calcaneum of *Dama dama*: note the pitting and scoring; C) *Equus ferus* unidentified fragment showing pitting and scoring; D) *Equus caballus* femur with a "cylinder shape" and crenulated edges; E) medial phalange of *Cervus elaphus* showing a puncture; F) left antler of *Dama dama* with gnaw marks; G) right metatarsal of red deer; H) left unidentified bone of *Equus ferus*. Scale= 1 cm (Arsuaga et al., 2012).

The fossils of **Navalmaíllo Rock Shelter** presented here were recovered between 2006 and 2014. The bones treated during these years came all from level F, which corresponds to the main occupation of the rock shelter by a group of Neanderthals. The best preserved fossils were fragments from large-sized mammals, especially cranial and appendicular bones with a predominance of long bones (Huguet Pàmies et al., 2010). The fractures, mostly of anthropogenic origin, are longitudinal with straight angles or curved with oblique angles. Anthropogenic marks have been documented, such as fractures due to impact and percussion in long bones (tibiae and metapodia from large and medium-sized animals); fractures due to flexion (peeling) in flat bones (caused during efforts to obtain nutrients); and cuts due to dis-articulation in the epiphysis. Surface analysis denotes scarce carnivore activity (Huguet Pàmies et al., 2010). Some bones associated with hearths present multiple fractures and a change in color caused by combustion. Lithic industries are very abundant and their state of preservation was relatively good in those elements, whose raw material consists of mono-mineral rocks (e.g. quartz, quartzite) or those that are predominantly composed of microcrystalline textures. However, lithic artefacts made of large-grain, poly-mineral rocks (i.e. gneiss) were not as well preserved. Abundant sediment concretion was often observed on the surface of the lithic artefacts, which initially hampered morphological determination and wear analyses until this concretion could be removed (Figure 7; Table 1; Huguet Pàmies et al., 2010; Márquez et al., 2013).

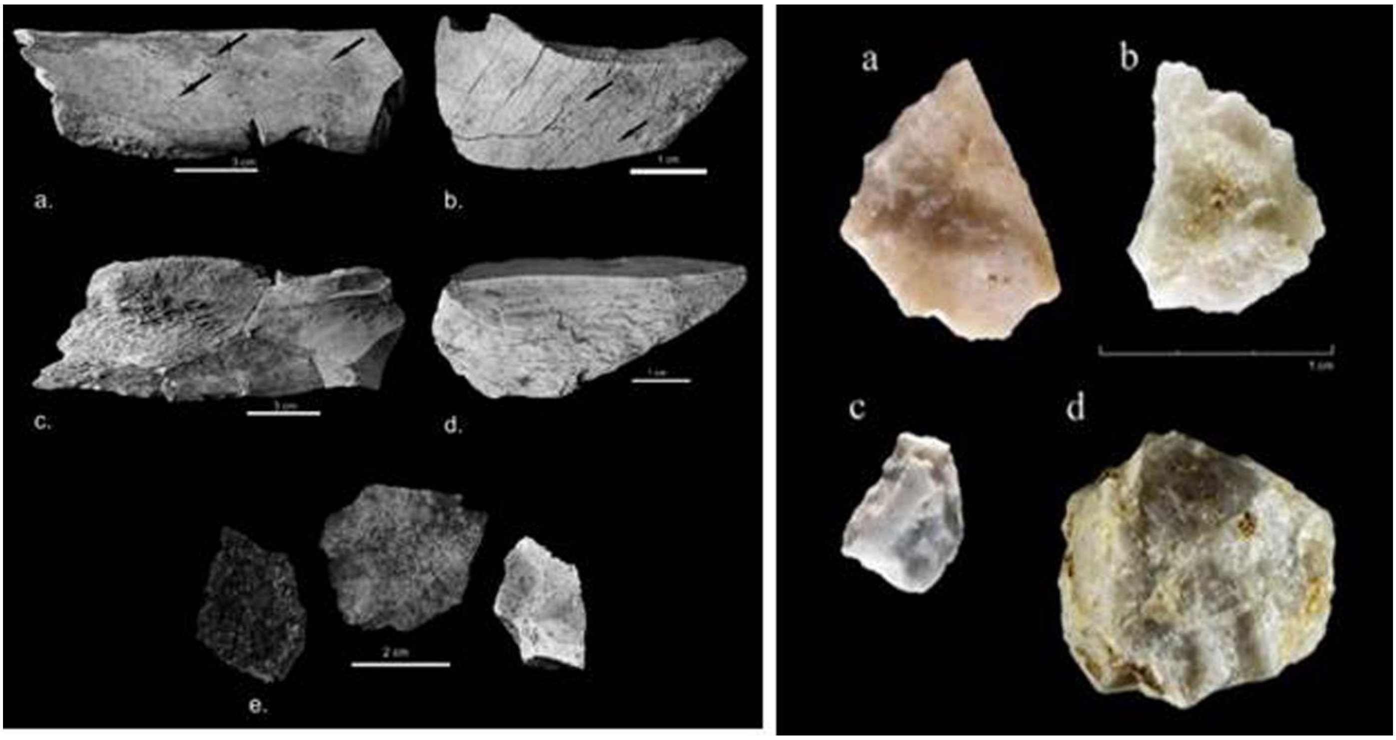


Figure 7 - Left: Evidence of anthropogenic activity in the Navalmaíllo Rock Shelter: A) and B) long bones of a large-sized animal with cut marks, C) long bone of a large-sized animal with anthropogenic fracturation, D) percussion cone, E) burned bones with distinct levels of blackening. Right: lithic tools manufactured in quartz from level F of the Navalmaíllo Rock Shelter: A and B) Denticulate tools, C) Sidescraper, D) Centripetal core (Huguet Pàmies et al., 2010; Baquedano et al., 2011).

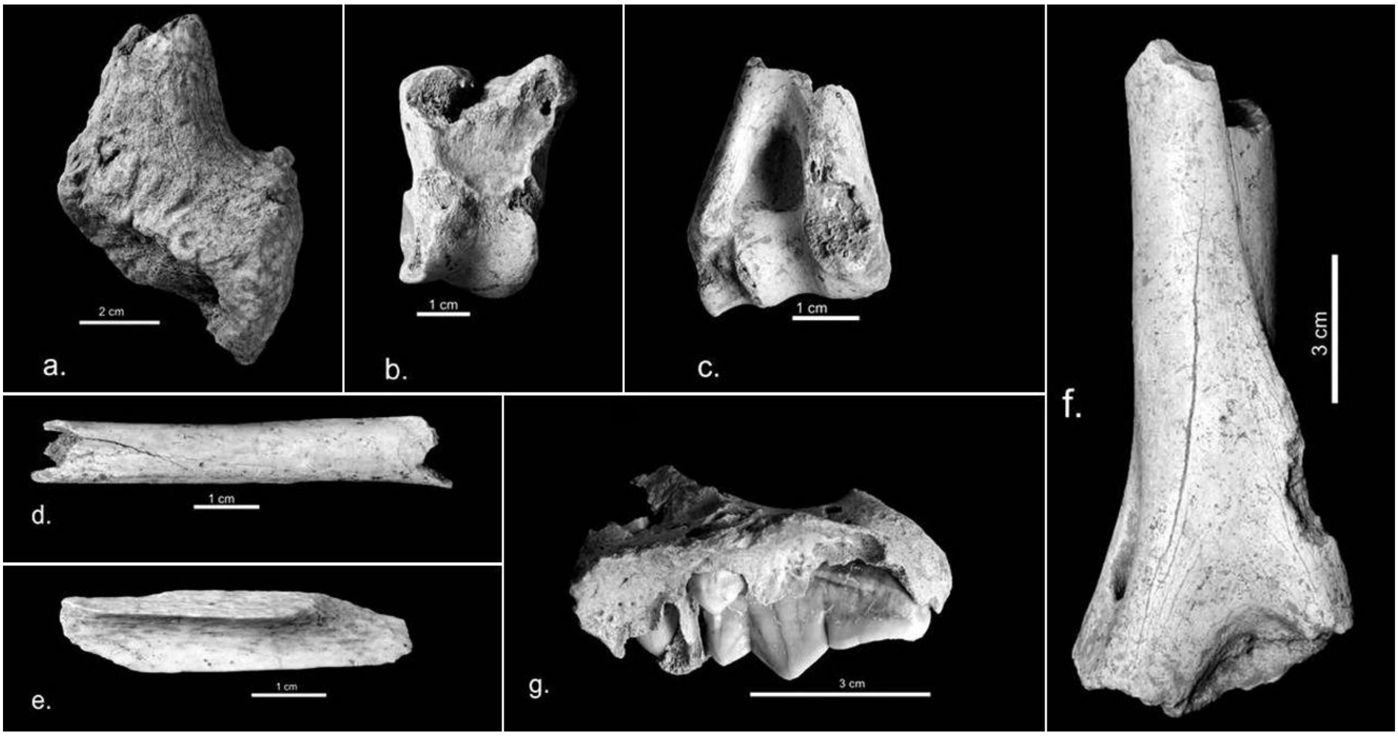


Figure 8 - Evidence of the presence of carnivores in Buena Pinta Cave: A) bitten and licked cervid antler, B) bovid phalange altered by stomach acids, C) bitten and fractured cervid humerus, D) Hyaenidae radius with diaphysary cylinder morphology due to the consumption of its epiphysis, E) fragments of a digested long bone, F) *Panthera leo* humerus with the distal epiphysis consumed and pitting on the diaphysis, G) fragment of a *Crocuta crocuta* maxilla. (Huguet Pàmies et al., 2010).

The fossils from **Buena Pinta Cave** considered in this paper were recovered between 2009 and 2014. The main occupation of this site was by carnivores, mainly hyenas (*Crocuta crocuta*; Huguet Pàmies et al., 2010; Baquedano et al., 2010, 2011), which modified the fossils characteristically.

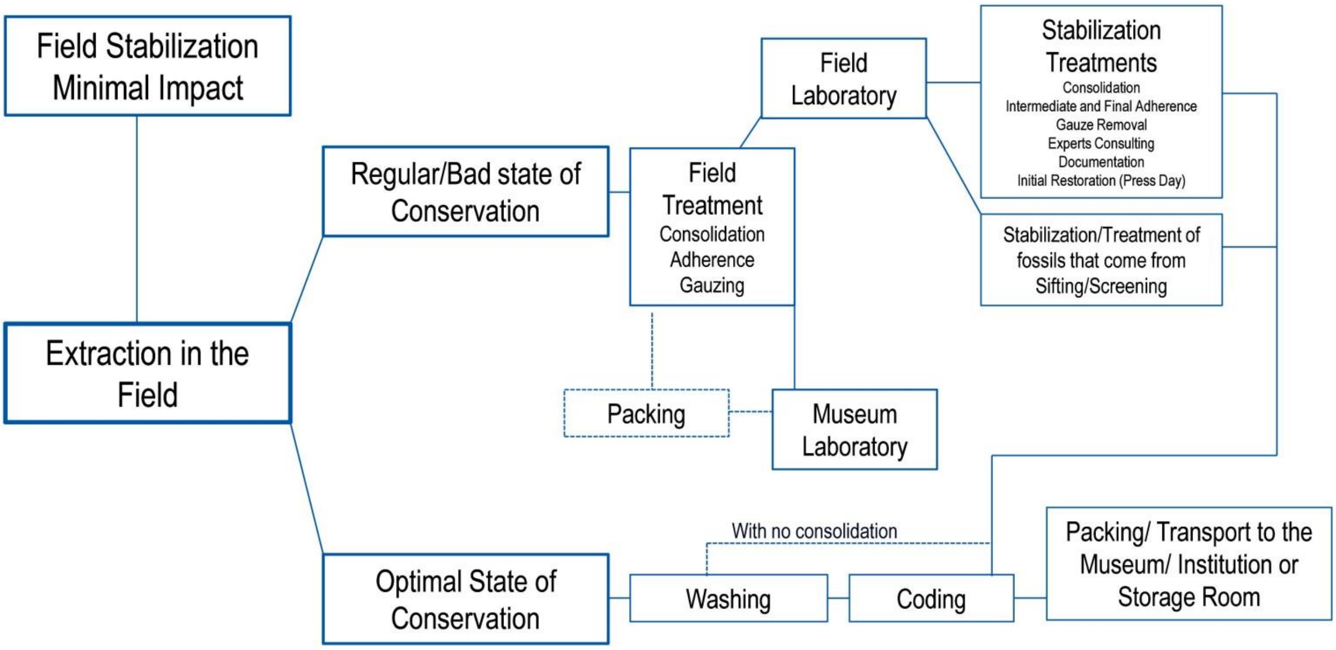
The fossils in the site, which in large part were of medium size (37.7%), consisted of fragmented bones; whole bones, carpals, tarsals and phalanges were scarce. Fractures were transversal with straight angles and irregular planes or longitudinal with straight angles and soft planes. Fractures made by carnivores were of a helicoidal shape, and puncture marks were also observed. Other marks include bite marks (scores, punctures), and marks caused by the action of digestive acids (crenulated and/or polished). Manganese oxide spots of a postdepositional nature were also present, and the longitudinal and mosaic cracking in the bones is due to differential changes in moisture (Figure 8; Table 1).

TREATMENTS

Intervention strategies on the sub-fossils undergo different stages: in situ intervention, treatment in the field laboratory, in the restoration laboratory or at the research center. The objective of these treatments is to prepare the bones for the performance of scientific studies on them and/or for their exhibition and display (Graphic 1).

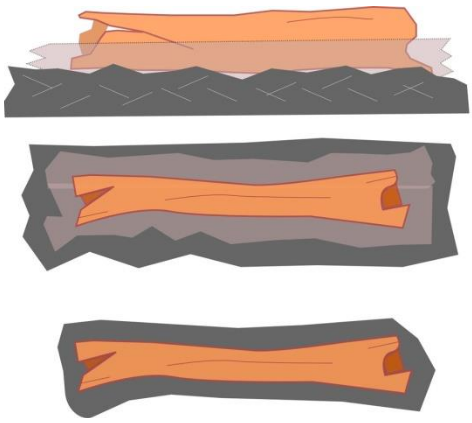
Table 1 - States of preservation/alterations associated with site and bone.

Site	State of preservation	Type of fossil	Main alterations
Camino Cave	Good	Teeth	-Fissures and fractures (abundant, especially transversal and longitudinal) -Crenulated edges -Polished surfaces -Root marks -Exfoliations -Carnivore marks (>70%): punctures, perforations, pits, scores -Manganese oxide spots
		Long bones lacking epiphysis	
		Small-sized bones	
	Fair	Long bones	
		Flat bones Cranial bones	
	Poor	Diaphysis Long bones Cranial bones	
Navalmaíllo Rock Shelter	Good	Frag. Long bone diaphysis Dental bones	- Decay associated with the small size of the fragments. Multifragmentation. - Anthropic marks: fresh fracture deriving from lamination. - Dark spots due to the presence of hearths and combustion. - Porosity -Manganese oxide spots
	Fair	Cranial bones	
		Appendicular bones	
	Poor	Small-sized bones	
		Flat	
Buena Pinta Cave	Good	Carpals/Tarsals/Phalanges	- Transversal and longitudinal fractures. - Carnivores: bite marks, scores, punctures - Digestion: crenulated and polished -Manganese oxide spots -Changes in moisture: longitudinal and mosaic cracking.
		Maxillaries/Dental pieces	
		Coprolites	
	Fair	Cranial bones	
		Flat bones	
		Appendicular bones	
	Poor	No remain is unrecoverable	



Graphic 1 - Material phases during excavation process and field laboratory.

Our main objective for treatments applied at sites during excavation is the stabilization of the fossils. A criterion of minimum intervention is followed from the very moment of discovery. In order to carry out scientific taphonomic and taxonomic studies, it is very important to quickly evaluate the state of conservation and/or decay in an individualized manner, and execute different processes accordingly. In some cases, the team will act on the entire fossil and in others just on certain isolated areas. These treatments consist of preventative gauze coatings and/or applying adhesive to surface areas (morphological conservation); isolated adhesion of fragments to avoid their dispersion and/or loss (facilitating the definitive adhesion in the laboratory); consolidation to maintain cohesion and mechanical resistance; and in all cases extraction with a packaging composed of tissue paper and aluminum foil as a kind of frame (Graphic 2). As a conservation strategy, an effort is made not to leave fossils on the surface from one excavation season to the next. In cases, where parts of some fossils remain in situ, they are protected by a gauze coating applied directly to the bone surfaces with Paraloid B-72® at 15% in acetone and/or consolidation, in addition to cover layers of geotextile and plastic to buffer against climatic variables.



Graphic 2 - Strategy for packaging the fossils at the site for their transfer to the field laboratory.

The materials were transferred to the field laboratory, where they were unpacked under controlled conditions for their acclimatization to their new environment. Later, a diagnosis is made, accompanied by graphic documentation. All of that is included in the project's common database, which is available for all researchers to consult. The bones receive intervention treatments establishing priorities, evaluating the resources at hand, including human and material resources, in addition to available time. Treatments that are carried out include: unpacking, cleaning (elimination of sediments and surface dirt), consolidation, adhesion of fragments and/or reconstruction and packaging for their transfer to the Museo Arqueológico Regional de la Comunidad de Madrid (MAR). The purpose of these treatments is to preserve as much information these fossils provide us as possible, respecting the surfaces so that they may be analyzed, adapted to each particular material and keeping in mind its state of preservation or decay. Use of chemicals is kept to a minimum, opting for compatibility and reversibility as in the case of the acrylic resin Paraloid B-72® (Storch, 1983; Koob, 1986; Johnson, 1994; Kres and Lovell, 1995; Down et al., 1996; Davidson and Alderson, 2009; Davidson and Brown, 2012; López-Polín, 2012) and occasionally cellulose nitrate (used for temporary adhesions in the field). Likewise, in the case of solvents, we always seek to use the least toxic: acetone, demineralized water and alcohol (Table 2).

Conservation treatments are performed alongside taphonomic and taxonomic studies, which are made possible by supplementary work performed by the interdisciplinary team. Multi-disciplinary work, in which a dialog amongst experts is established, takes place during the reconstruction treatments, the taphonomic interpretation of the decay of the fragments, and later during taxonomic studies. Finally, the bones are deposited in the MAR. We then proceed to revise the sub-fossil and their documentation. Initial treatments are supplemented, and treatments that had been impossible to apply in situ are performed. In each case, the intervention is carried out considering the stability of the bones and their needs in order to maintain all the information needed for scientific studies, and allowing for their exhibition and dissemination in society. The examples discussed in this article are a representation of the different interventions carried out on bone materials at three analyzed sites.

Here we describe in detail the procedures applied to some of the fossils from the Camino Cave, Navalmaíllo Rock Shelter and Buena Pinta Cave sites in Pinilla del Valle.

Table 2 - Summary of the different treatments applied to the fossils at the sites of Pinilla del Valle.

Treatment/ Context	In situ	Field laboratory
Consolidation	- 5% Paraloid B-72® in acetone - 10% Paraloid B-72® in acetone (Very decayed) - Undiluted cellulose nitrate. Surface union of fragments in situ by way of protective film the adhesive. It can be reinforced with gauze on the surface as a kind of hinge. - Paraloid B-72® at 50% in acetone.	-3% Paraloid B-72® in acetone -5% Paraloid B-72® in acetone
Gauze Coating	-10% Paraloid B-72® in acetone with organic gauze (different since, maximum adaptability). -20% Paraloid B-72® in acetone (second layer, maximum resistance)	-10% Paraloid B-72® in acetone with gauze. In case the sub-fossil is transferred to an institution's laboratory, given its fragility.
Adhesives	Cellulose nitrate	- Adhesive HMG Paraloid B-72® in tubes. - Paraloid B-72® at 50% in acetone.
Cleaning	Mechanical dry cleaning: paintbrushes, brushes, orange tree stick, bamboo stick, dental tool	Mechanical dry cleaning: paintbrushes, brushes, orange tree stick, bamboo stick, dental tool, micro lathe, ultrasound, engraver. - Chemicals/Mechanical wet cleaning. Water: Alcohol (1:1), Alcohol, Acetone (for previously consolidated bones).

CAMINO CAVE: CASE STUDIES

In Camino Cave, the selected fossils are found complete or almost complete, piled on top of one another, which complicates their extraction. Furthermore, in some cases, they are much fractured and after taking off the sediment, the fragments detach, causing significant loss of taphonomic and taxonomic information (Figure 9). In order to perform taphonomic analyses on the bones as a whole, they must stay in position for some time to accurately establish the topological relationships among the distinct elements. For the purpose of taxonomic analysis, extracting the bones is essential in order to study the marks on their surfaces. In many cases, this particularity implies the need to place occasional isolated gauze coverings or line-of-sight surface coverings to stabilize the morphology.

Below, we describe some examples of intervention in situ belonging to levels 3-5 of the central sector (Figure 3) and in the field laboratory at Camino Cave.

Metapodial of Equidae

Here, we present a complete metapodial from an adult individual from the 2009 excavation season. The state of preservation was poor, with several old fractures. One fracture was transversal, approximately halfway through the diaphysis, separating the fossil in two main parts, which changed the angle of the slope on two planes. Additionally, the metapodial exhibited various longitudinal fractures that ran along the length of the bone, leaving fragments joined together by sediment; bone material was missing in an isolated area of the distal diaphysis. Sediment had adhered to the surface and also in the interior of the bone (Figure 10).

After evaluating the state of the decay, it was decided to place gauze coating on the two parts of the bone. Before carrying out this process, the bone surface was consolidated with Paraloid B-72® at 5% in acetone. The gauze coverings consisted of cotton gauze strips of varying sizes applied in a criss-crossed manner (which facilitates its removal) with B-72 consolidant at 10% and 15% in acetone (Figure 10A). In some cases, the team was unable to place the gauze coverings all at once and so this was done over time as the fossil was being excavated. The need to visualize the fossil with respect to the entire set of bones from this area, in order to carry out taphonomic studies, caused the gauze covering to be removed at a certain time. To that end, we dissolved the consolidant adhering the gauze to the surface with a paintbrush, until the different layers of the coating separated (Figures 10B, 10C). The gauze coating on the largest-sized fragment was removed without difficulty. However, the smaller assemblage of bones fragmented during that process (Figures 10D, 10E). Therefore, this assemblage was extracted, the sediment from the bone's interior and cortex was removed, and the fragments were consolidated and joined with cellulose nitrate adhesive in situ (Figures 10G-I). Finally, this fragment was returned to its original position in the site so that all the relevant studies to be conducted (Figure 10J).

Figure 9 - Left: Accumulation of fossils in squares C3 and D4, some bones are partially covered in gauze during the 2008 excavation season. Right: A large accumulation of long bones is shown in detail (at least three metapodia are represented), which is characteristic of the central sector (pulled apart 1, Figure 3). Scale in centimeters (Arsuaga et al., 2012; Photos PVRT).

Figure 10 - Different stages of the conservation processes in situ: A) gauze coating, B, C, D, E and F) removal of the gauze, G and H) cleaning and J) reconstruction of the Equidae metapodial in situ (Photos PVRT).

The results were good, though it is unusual to place gauze coatings and remove them from fossils in situ. Finally, the metapodial was moved to the laboratory for cleaning with acetone, which served to remove adhesive residue as well as the consolidant from the surface, after the placement of the gauze coating. In this case, the reconstruction - the joining of both parts - was interrupted by taphonomic studies.

Humerus of *Bos primigenius*

The following case is a complete *Bos primigenius* humerus from an adult individual recovered during the 2006 excavation season. The state of conservation of the fossil was regular. Some of the bone material was missing: the proximal epiphysis and certain areas of the distal epiphysis (where the condyles are located). It had old fractures in different areas: one longitudinal, which ran along the length of the fossil on both sides and another that was diagonal in the diaphysis and filled with sediment. Furthermore, the most proximal fragment showed several fractures with distortions (Figures 11J-K). This breakage could be due to continuous pressure, leading to an internal microfragmentation. There were also fractures in the distal epiphysis, which hindered the maintenance of its complete morphology during the extraction process.

After considering the general condition of the bone, it was decided to partially coat the fossil with gauze in isolated areas on both ends in order to render the recovery possible. Very specific areas were gauzed: the distal epiphysis and the diaphysis from mid-length to the near end in order to support and restrain the fragments as much as possible (Figures 11A-C). In order to avoid possible morphological losses, the object was extracted together with the sediment, supporting the fossil with aluminum foil to ensure integrity until arrival at the field laboratory, where the packaging was removed and the sub-fossil documented, carrying out a new appraisal of its state of preservation (Figure 11D) after extraction - in accordance with our protocols. In the laboratory, it was decided to eliminate the sediment from the surface and stabilize the fossil (Figures 11F-I). No other intervention was carried out, since the fossil was scheduled for taphonomic studies (Figures 11J, 11K).

Figure 11- Humerus of *Bos primigenius*, A) superior views view of the fossil in situ with occasional gauze; B) and C) different views of the fossil covered in gauze at the site; D) top view of the fossil as it arrived at the field laboratory; F) bottom view of the humerus with the sediment before the intervention; G) detail of the sediment in the proximal epiphysis before being cleaned; H) detail of the cleaning, mechanical elimination of the sediment at scalpel point; I), J) different views after the elimination of the sediment; K) detail of the fracturation in the distal diaphysis (Photos PVRT).

Crocuta crocuta hemimandible

This case is an example of minimum intervention, which involves a right mandible from an adult hyena, *Crocuta crocuta*, from the 2007 excavation season. The mandible had longitudinal fractures joined together by hardened sediment and another transversal fracture that separated the fossil in two halves. It was extracted in two parts with abundant sediment on one of its sides (Figures 12A-C). It was unnecessary to consolidate it or cover it in gauze, since the sediment worked to cement it and the bone material was found in a very good state of preservation. After its transfer to the laboratory, some mechanical cleaning work was conducted with a scalpel point, wetting the sediment surfaces with demineralized water, leaving the fossil pristine for its taphonomic study and subequent definitive adhesion (Figures 12E-H).

NAVALMAÍLLO ROCK SHELTER: CASE STUDIES

Below are some examples of both in situ interventions and interventions performed subsequently in the field laboratory at Navalmaíllo Rock Shelter. At this site, complete fossils were scarce. Most of the bones were fragments, and were mostly teeth of large-sized fauna. There were accumulations of bone fragments in isolated areas of the site. Some accumulations were found in hearths. Thus, maintaining them in the site was important in order to conduct scientific studies, particularly taphonomic studies.

Ruminant atlas

The following case is a description of the intervention carried out on a complete atlas belonging to an adult individual of a ruminant from the 2010 excavation season. This sub-fossil had old fissures and fractures in all directions, most of which were supported by sediment. It was extracted from the site with excess sediment, especially in the foramen (Figures 13A, 13B). It was transferred to the laboratory and, after performing an organoleptic exam with optical magnifiers, cleaning treatments took place. The sediment was eliminated by wetting it with water to soften it and extract it mechanically with a scalpel point, and then with a wooden toothpick once closer to the bone surface (Figures 13C, 13D). Afterwards, it was consolidated with Paraloid B-72® at 5% in acetone using a syringe on the interior and permeating the exterior of the fossil (Figures 13E-G).

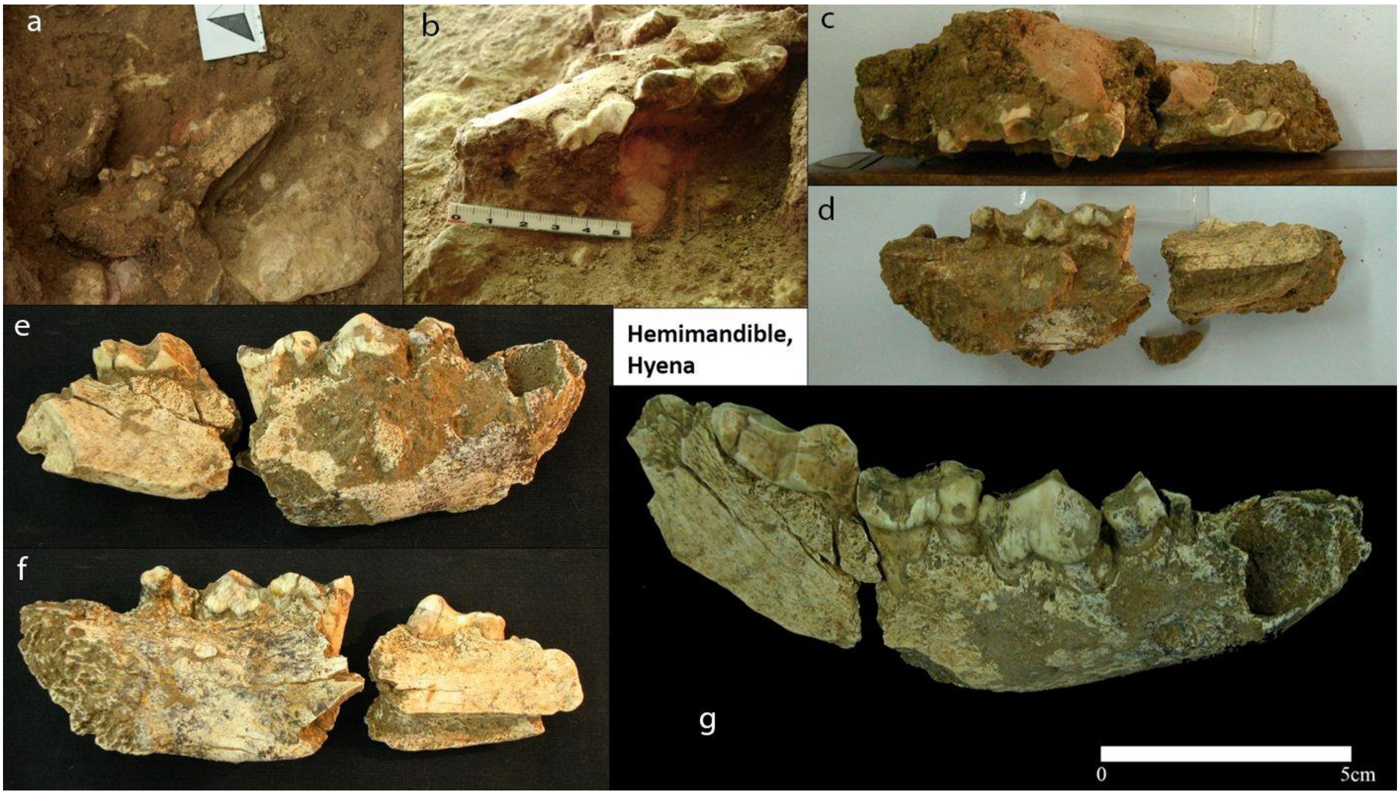


Figure 12 - Hyena *Crocuta crocuta* right hemimandible. A, B) Two views of the fossil in situ at the site; C, D) superior and lateral views of the fossil with the adhering sediment before cleaning; E, F) lateral and medial views during the cleaning process and G) the hemimandible after cleaning and reconstruction (Photos PVRT).

Figure 13 - Complete vertebra. A) sub-fossil before restoration; B, C, D) cleaning processes; E, F, G) after intervention in the field laboratory (Photos PVRT).

Upper right premolar of a large bovid (Aurochs or *Bison*)

The following is a description of the intervention carried out on a premolar from a large bovid, comprised of 12 fragments. It was found in square B21 during the 2010 season. This tooth displayed old fractures and surface dirt. Conservation treatments performed were minimal: cleaning with water and reconstruction with Paraloid B-72® adhesive at 30% in acetone (Figure 14). Conservation work served to identify the taxon.

Figure 14 - Premolar of a bovid (Aurochs or *Bison*), left: fragments before of the restoration, and right: reconstruction of a dental piece from square B21. (Photos PVRT)

Figure 15 - Left: Ground location of the bone accumulation in square C18 of the Navalmaillo Rock Shelter site. Right: A) detail of the bones before the intervention; B) consolidation and adhesion of fragments of a fossil in situ; C) detail after the adhesion and consolidation; E-F) gauze treatments on two bones; G) final view of the fossils after the intervention.

Bones in square C18

Here, we will discuss a group of bones exposed in square C18 during the 2014 season (Figure 15, left). This is a set of bone fragments possibly belonging to different individuals. The state of preservation of some of them was regular as they presented old fractures, laminations and fissures, as well as some recent fractures. There was sediment between the fossils (Figure 15A). The team opted to demarcate each bone fragment and later individualize the treatments. Regarding the bone fragment located in the center (the largest as observed in Figure 15A), consolidation with Paraloid B-72® at 5% in acetone applied with a syringe on the interior, and permeating the exterior of the fossil of consolidant with Paraloid B-72® at 15% in acetone was decided upon in order to avoid further decay, as well as to join the fragments with new and old fractures to avoid displacements (Figures 15B, 15C). In the other two cases, the decision was made to coat them with gauze, one in an isolated area and another on all visible bone surfaces. These treatments were performed to avoid the loss of fragments (Figures 15E-G). The fossils were extracted separately and transferred to the laboratory.

The results were good as the bones were stabilized by the treatments performed (the consolidation, adhesion and gauze) and losses were avoided. In this square, four fossils received interventions out of a total of 92 that were found; thus, intervention was minimal.

Accumulation of bones in square B20

An accumulation of bones was found in 2014 in square B20. This included an assemblage of bone, lithic and blackened limestone fragments, small in size, most of them burned, which were believed to belong to a hearth. All of the bones were found thermally altered (Figures 16A-C).

Their state of preservation was generally poor. Different levels of decay and alterations on the bones were present, e.g. discoloration produced by combustion (darkening of the bone surface all the way up to complete blackening, even calcination; Figure 16F). In addition, the bones were found fractured, fissured, with root marks, etc. Due to the delicate state of preservation of some of the bone fragments, not all could be saved; therefore, it was necessary to collect information about the set in the site itself. At the end of the 2014 season, there had been one day of torrential rains and, despite having covered the site with plastic tarps, the water penetrated the site and carried the sediment and some materials all over the square from North to South, causing some dislocation. The square was left to dry at ambient temperature for two days, after which it was confirmed that some bones could not be saved (Figures 16D, 16E).

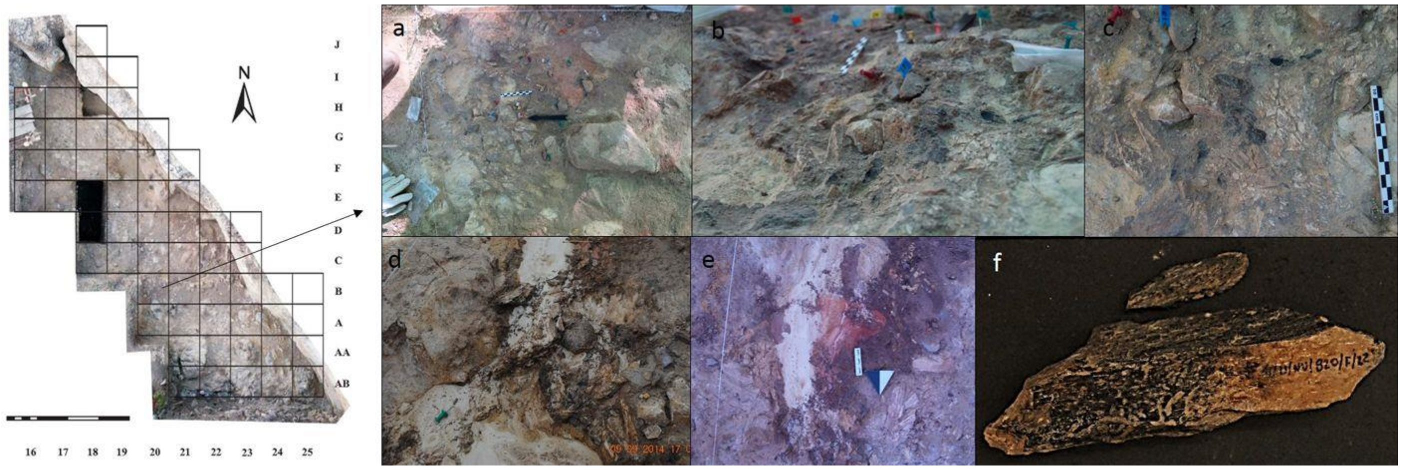


Figure 16 - left: ground location of the accumulation of bones from the possible hearth in square B20 of the Navalmaillo Rock Shelter: A) superior view of the square; B) and C) details of the hearth with the lithic and bone; D) and E) details of the square after a big storm; F) remains of a bone fragment with discoloration caused by fire after treatment.

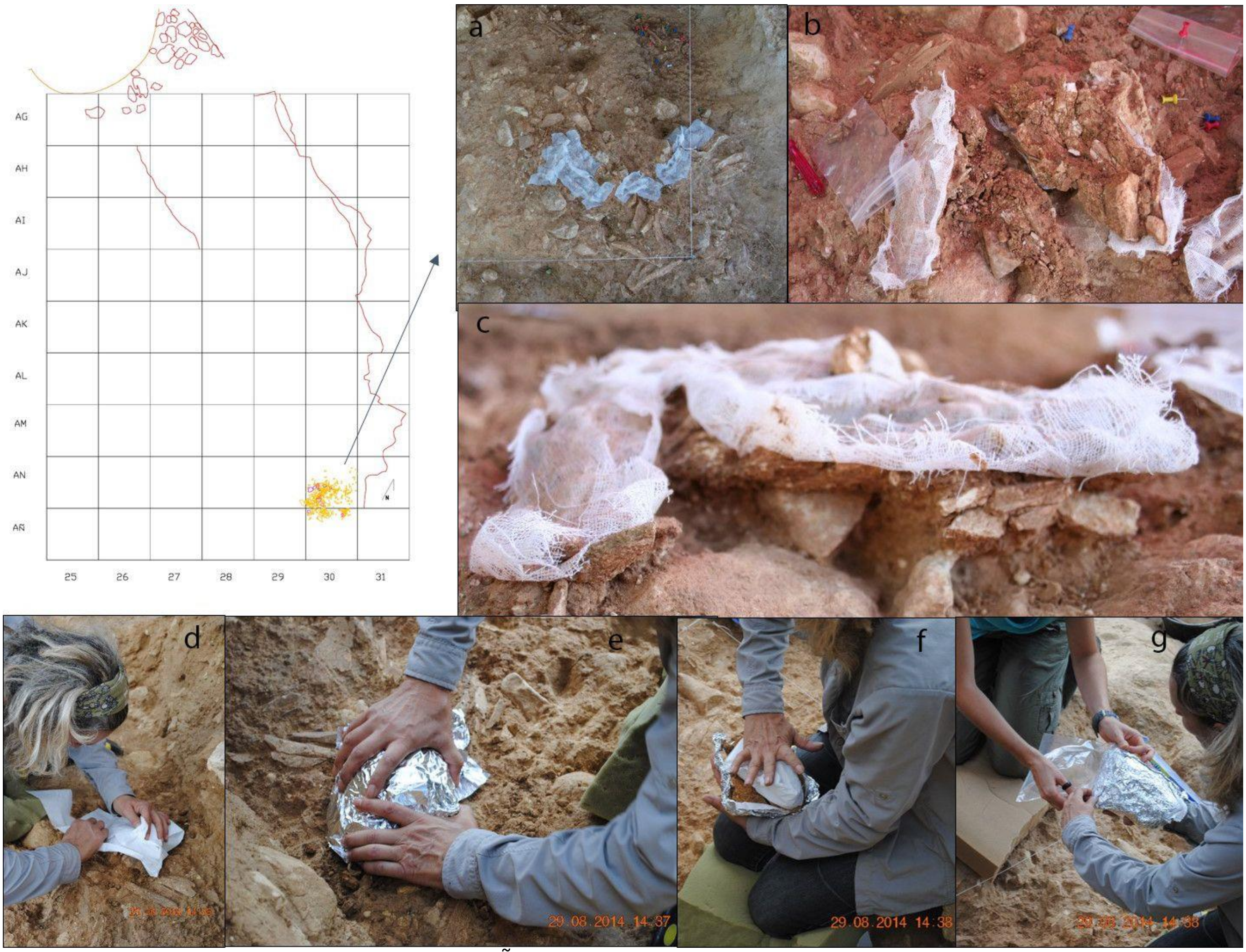


Figure 17 - Assemblage of bones in squares AN-AÑ 30. A-C) Views of the gauzing procedures and D-G) extraction of some fossils during the 2013 campaign. Fossils as they arrive at the laboratory (Photos: PVRT).

Assemblage of bones in squares AN-AÑ 30

In this last case, we will discuss another concentration of bones (accompanied by lithic finds): the bone assemblage in squares AN-AÑ 30, exposed during the 2013 and 2014 excavation seasons. This involved a set of fragments, especially parts of a diaphysis of a long bone (Figures 17, 18). They were found at different orientations and slopes. Some were piled up and/or superimposed. Most of the fossils exhibited fissures, laminations, and old fractures with imbricated sediment. The fractures were longitudinal, transversal and diagonal. In many cases they were very small, which is why, during the excavation, fragments tended to separate from the set, which resulted in bone decay and loss of information (Figures 17, 18). In this case, the state of preservation was evaluated as the bones were exposed. At the outset, it was decided to place gauze on those bones that were found in the worst state of preservation (Figures 17A-C) in order to facilitate continuity in the excavation work. Later, they were collected and wrapped in tissue paper and aluminum foil to properly support the fossils, and they were placed in a perforated polyethylene bag with an identification tag for their transfer to the laboratory (Graphic 1; Figures 17D-G).

The importance of this assemblage and its resulting taphonomic study required that the bones remained in situ. However, application of gauze in the other cases would have prevented a complete interpretation of the context. Therefore, rather than placing gauze on the bones in the following interventions, we opted for applying an adhesive layer (cellulose nitrate or Paraloid B-72® at 40-50% in acetone) on the surfaces in the following interventions to protect the bone surfaces, as well as to keep them in their positions, allowing a complete interpretation of the context and future taphonomic studies (Figures 18B-H). All of these processes were accompanied by exhaustive graphic and photogrammetric documentation.

This assemblage suffered the consequences of a large storm that caused mud to infiltrate many areas of the site at the end of the 2014 season. Squares AN-AÑ 29-30 was covered in mud despite the site being covered by plastic tarps (Figures 18A-D). After assessing the damage, it was decided not to excavate for two days and to leave them uncovered to air-dry (Figures 18I, 18J). In the following, the mud covering the surface was removed, using wooden toothpicks to prevent damaging of the bone surface. In some cases, ethanol was applied to the bones by dripping to accelerate evaporation and to remove moisture from the fossils. Once they were dry, they were extracted from the site, leaving only the bones at the center of the excavation in situ (Figures 18I-L, bottom).

Figure 18 - A) Assemblage of the bones and lithic in AN-AÑ 30 from the Navalmaíllo Rock Shelter site. B-D) Details of the state of conservation e) Bones and lithics during process of excavation. F-H) Details showing the highly fragmented bones I) Detail of the working area after a storm J) Bones in mud after the storm. K) Removal of mud. L) Assemblage de bones and lithic after mud removal in 2014 (Photos PVRT).

Most of the treated fossils were extracted without difficulty. The bones that remained on the surface were protected with geotextile, Arlite®, and expanded polyurethane. Thanks to the treatments, taphonomic and archeological studies were made possible.

BUENA PINTA CAVE: CASE STUDIES

Some examples of interventions in situ at the Buena Pinta Cave and at the field laboratory are described. Bone representation at this site was fragmentary, with very few complete bones: tarsals, carpals and phalanges, as well as an occasional mandible.

Maxillary fragment of a hyena (*Crocuta crocuta*)

The first example presented from this site is a maxilla of the species *Crocuta crocuta* (hyena), from an immature individual, exposed during the 2006 excavation season. The bone had sediment on its surfaces along with root marks (Figures 19A, 19B).

Stabilization treatments performed to conserve it for its future study included local cleaning with demineralized water, without completely submerging the fossil, and surface consolidation (Figure 19). This case did not present difficulties, but the importance of the fossil made a taxonomic study essential.

Tortoise shell fragments

On the last day of the 2013 season, fragments of a tortoise shell and a long bone were exposed in square G51. The team opted not to retrieve them because it was suspected that there would be more fragments belonging to the same individual. The fragments were protected by applying Paraloid B-72® at 30% in acetone to the surfaces (Figures 20C-F). Finally, they were covered with geotextile. At the beginning of the 2014 season, the site was uncovered and the fragments were found. Subsequent work revealed numerous fragments belonging to the same fossil. All of the fragments were left in situ until a sketch was made for future handling and studies. Then they were extracted and packaged in independent polyethylene bags, accompanied by identification tags (Figures 20G-I).

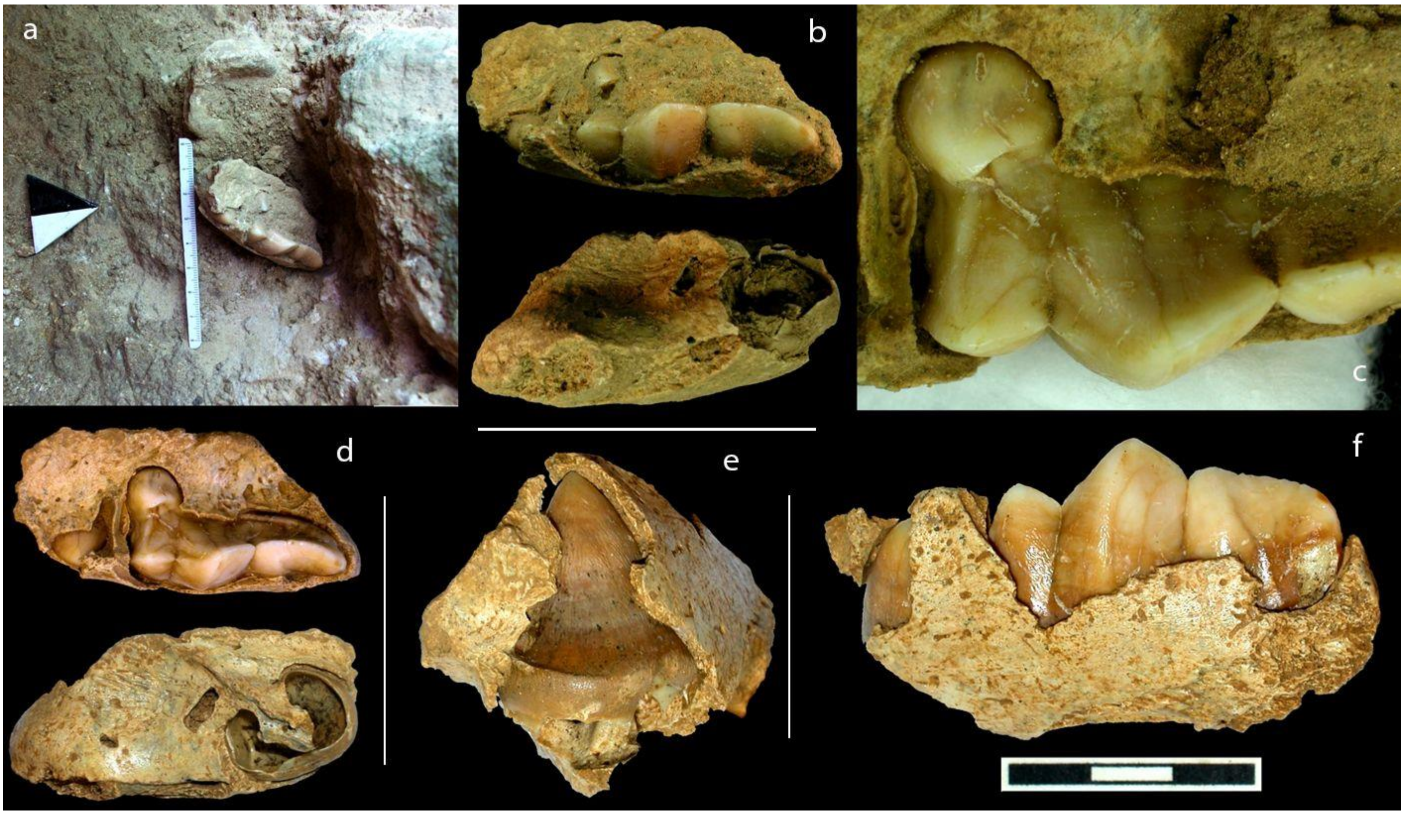


Figure 19 - Hyena maxilla. Minimum intervention during a conservation process; excavation, cleaning and consolidation in 2006. A) Maxilla during excavation process; B) Top and bottom view before conservation treatment; C) Cleaning process detail; D-F) Views after conservation process (Photos PVRT).

Figure 20 - Tortoise fragments. A,B) Excavation process; C-F) Temporary coating with cellulose nitrate applied in 2013; G-I) Fossil fragments undergoing the excavation process in 2014; J) Fragments after excavation (Photos PVRT).

Figure 21 - A-C) Bones in situ: maxilla, vertebra, long bone and vertebra; D-F) Bones after their extraction with sediment; G-I) Cleaning processes (Photos PVRT).

Maxilla, vertebra and long bone fragment of *Equus hydruntinus*

The set of bones from *Equus hydruntinus* (Hidruntinus) is composed of a maxilla, a vertebra and a long bone fragment from the 2009 excavation season, when they were found piled up in the NW corner of square J52. There were several fragments with old fractures held together by sediment (Figures 21A-C). The treatments of these fossils were performed in three stages: excavation in situ, elimination of the sediment in the field laboratory, and cleaning and reconstruction in the research center laboratory, which allowed for their recognition as three bones (Figures 21-23).

On site, the team decided to extract the bones in two stages: first, the exterior part of the maxilla with the teeth attached and second, the rest of the assemblage, with excess sediment to prevent fragments from detaching (Figures 21A-C). They were packaged and moved to the field laboratory, where the excess sediment was eliminated and all the fragments were separated from each other (Figures 21D-I). They were packaged and then brought to the research center, where cleaning treatments with demineralized water were performed. The teeth were cleaned by submersion, but the bone fragments were cleaned with a paintbrush to minimize the addition of moisture and to facilitate their drying. Once they were dried at ambient temperature in a controlled manner (avoiding heat from the light). They were consolidated and reconstruction commenced on each bone separately (Figures 22, 23A-C).

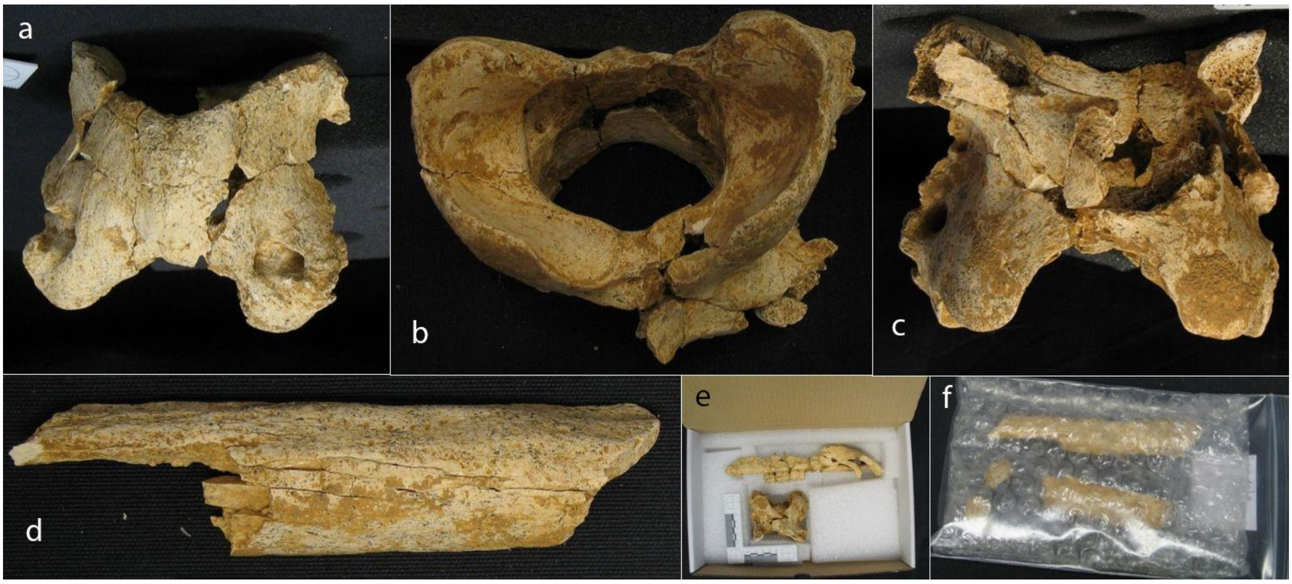


Figure 22 - Different views of the vertebra (A-C) and the long bone (D); E-F) packaging after their intervention of vertebra and long bone of *Equus hydruntinus* (Photos PVRT).

Figure 23 - Maxilla of *Equus hydruntinus.* A-C) Assemblage process; D-G) Maxilla after the conservation process (Photos PVRT).

The results were optimal, as it was possible to conduct taxonomic studies. Consequently, a first vertebra (atlas; Figures 22A-C), a diaphysis of a long bone (Figure 22D), and a maxilla (Figures 23D-G) of a horse were identified as belonging to the species *Equus hydruntinus.* After the study, the maxilla became part of a permanent collection at the MAR in Alcalá de Henares.

PREVENTATIVE CONSERVATION AT THE PINILLA DEL VALLE SITES: STATISTICS AND SPATIAL CONSERVATION.

In this brief section, some data will be presented, as well as the first conclusions concerning a conservation methodology that is starting to be applied in the field of conservation, and which we hope provides good results in upcoming on site work during excavation. It is important to highlight the documentation of the work carried out in the field laboratory. The processes associated with conservation are conducted in the field and they are recorded in a log that, in turn, is integrated into the excavation's general field log. The information collected in the log is associated with extractions, bones that will remain in situ, water run-offs, changes in sediment (geological/archaeological levels) or any unforeseen event that must be noted for future study.

In the laboratory, we work with a FichaModelo© (Model Form) modified from the Atapuerca team that is integrated into a general database. Thus, relevant information about each fossil, including archaeological, paleontological, taphonomic, and conservation information, is always kept together, which facilitates interdisciplinary work. For us, this is a key factor for creating preventative strategies.

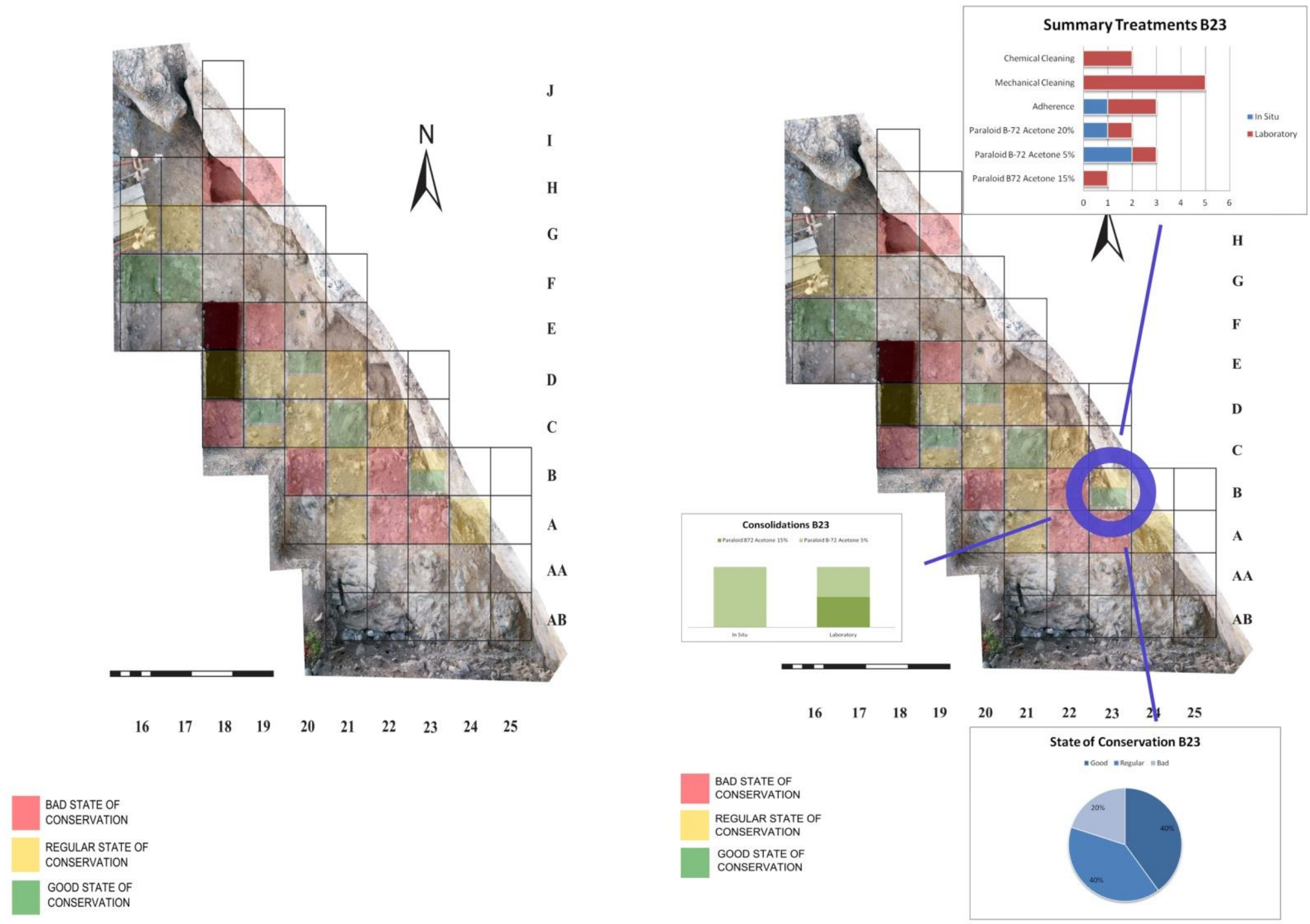


Figure 24 - Left. Mapping of conservation on the grid of the North Navalmaillo site mapped according to the statistics of the fossils treated there from 2006 until 2014 (Survey PVRT adapted by the authors). Right. A methodological example of an analysis of different conservation factors that define the state of preservation of bones in square B23 of the North Navalmaillo site.

Members of this team already presented this format at the past CotArq Conference (Other Archaeologies; Pastor Pérez and Canseco Domínguez, in press). In this regard, we have developed a method, which we call "spatial conservation" that combines the use of GIS with statistics applied to conservation-restoration interventions, allowing for mapping by area in each of the sites (Figure 24).

For this mapping, which is still in experimental stages, different variables are taken into account, and are combined to designate a risk level in each one of the squares in our sites. To work with this data, we have chosen a Northern sector of the Navalmaillo Rock Shelter and calculated the statistics in accordance with the fossils that have been treated, because, for us, this is more representative from a risk assessment standpoint (this can also be done following other criteria).

There are various possibilities since we also provide an analysis by square (Figure 24, left), comparing different treatments applied to the same elements: consolidation in situ or in the laboratory, states of preservation, or the total amount of treatments carried out on the finds / objects from a quantitative point of view (Figure 24, right). Furthermore, we can make comparisons among squares and work with the chronological variable to plan upcoming seasons ahead of time.

As can be observed in the figures, not all of the squares can be mapped because in some cases, there are not enough samples available for study, mainly because the state of preservation of most of the fossils does not require any treatment.

Working with the same tools used by our teammates, such as archeologists and paleontologists, facilitates conservation work at all levels and improves communication between different specialists. All of these actions have a very positive impact on the conservation of the extracted materials.

RESULTS

To conclude, we present a synthesis of the methodology followed by this team since 2006, which was when the current restoration team started. In the analysis, the number of excavators and sites excavated annually must be kept in mind. The opening of a new site, Des-Cubierta Cave, in 2009, and the need to broaden the areas of excavation caused us to reconsider the need to increase the number of people participating in the excavation seasons each year. In other words, in 2006, the team was formed by approximately 20-25 people, of which two or three were from the conservation team. The members of the team progressively increased until reaching its current size of approximately 80 people, of which between six and ten were conservators in 2014. These data are reflected in the increase of extracted materials and therefore the increase in fossils, along with the resulting conservation treatments.

A constant factor in our work at these sites is the completion of organoleptic analyses on the state of conservation before, during and after excavation in the laboratory; it is a system that is not only used to evaluate the state of the fossils, but also to evaluate the treatments we perform on them.

As we have seen over the course of this work, the pathologies that are produced in each one of the three sites are very distinct, just like each fossil found there, depending on its positioning and morphology. Each one of the discussed interventions is conditioned by multiple factors. Fossil recovery with minimum intervention and the preservation of the integrity of all parts of the bones is our main priority/objective, but in each case, we must adapt to the rest of the team's needs. When contemplating the study of the position of a bone deposit, we consider block consolidations or extractions, in which we use more chemicals.

On the contrary, when we have to extract a fossil from an assemblage, we opt for isolated consolidation or temporary adhesion, which facilitates its reconstruction in the laboratory. We constantly rely on sketches of the objects, made on polyethylene film, or on colored photographs. All of this documentation later accompanies the object to the laboratory or to its definitive storage, facilitating its future

Findings by Site (2006-2014)

	Camino Cave	Buena Pinta Cave	Navalmaíllo Shelter
2006	765	881	2598
2007	510	656	3291
2008	359	849	4625
2009	222	998	4510
2010	0	1256	1425
2011	0	745	2163
2012	0	894	1350
2013	0	750	2778
2014	0	1044	3339

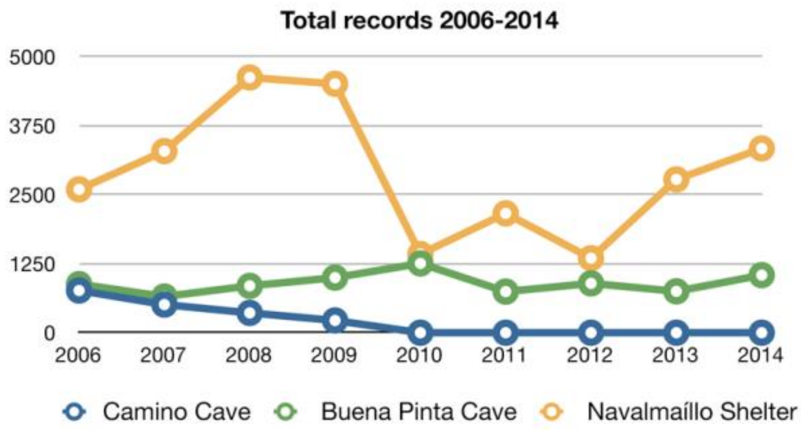


Figure 25 - Total number of specimens recorded between 2006 and 2014 in Camino Cave, Navalmaillo Rock Shelter and Buena Pinta Cave. The Pinilla del Valle database allows us to create graphics that facilitate easy consultation and comparison of data.

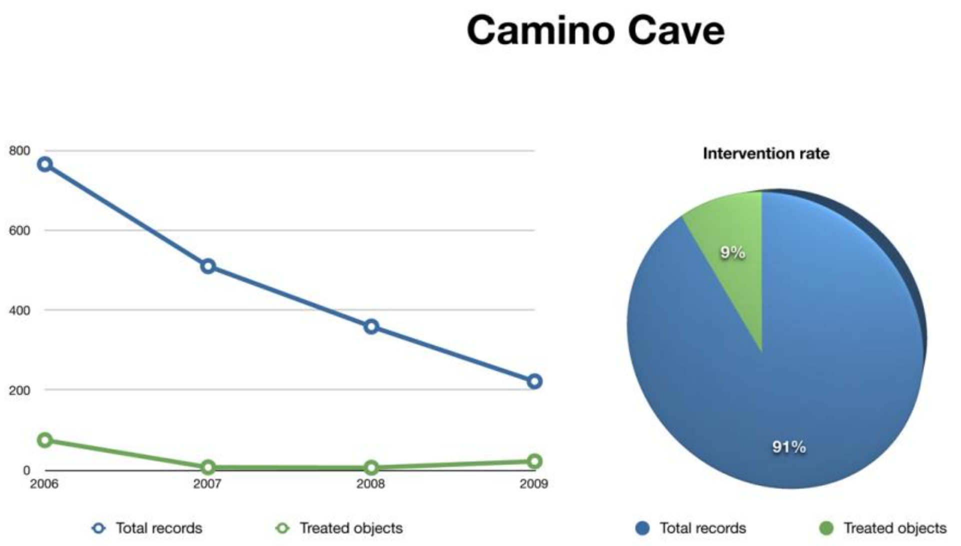
review. In many cases, it becomes necessary to leave the fossil semi-exposed until the following season, which forces us to place high resistance gauze coatings as well as a protective framework with polyurethane foam which, when mixed with Arlite®, provide a buffer against climatic effects and the presence of snow during the winter in the Lozoya Valley.

The effectiveness of the conservation strategy implemented by this team between 2006 and 2014 is analyzed below (Figure 25). The database represents the state of conservation for a total of 36,011 records, with only 450 cases (1.25%) of in situ intervention and/or field laboratory treatment. These data confirm that in the cases, in which the archaeological and/or paleontological materials have been treated, the principle of minimum intervention has also been followed, meaning that preventative or curative conservation processes took precedence over those of restoration.

Camino Cave, as we have seen, presents its own issues within the sites of Pinilla del Valle due to the large amount of complete fossils recovered. The supervision of each and every one of the 1856 objects has been constant, which has allowed us to reduce direct intervention to the indispensable minimum: in this case, just 110 fossils (9% of the total; Figure 26). This represents the highest percentage out of the three sites and it mainly encompasses actions associated with the consolidation and placement of gauze on the materials in situ allowing for information to be preserved that otherwise would have been lost in the process of excavation and study.

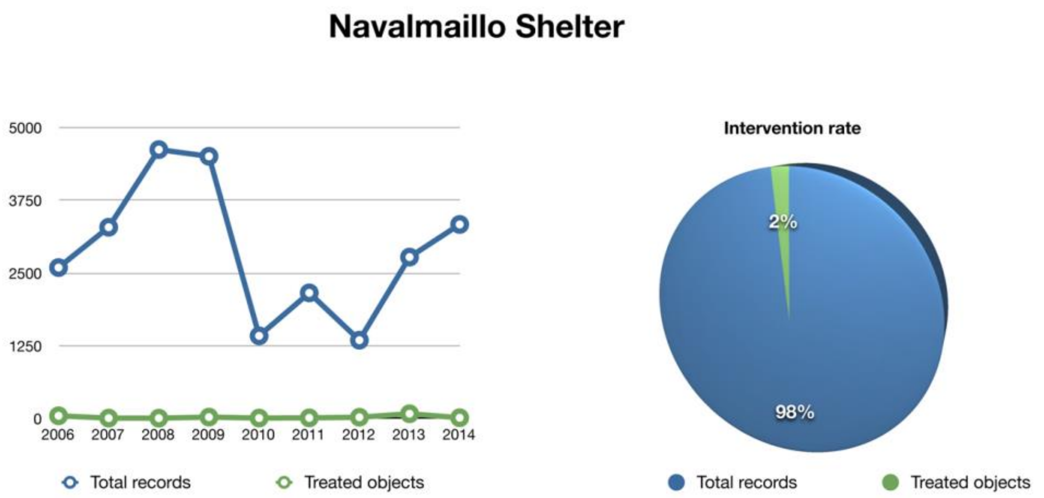
At Navalmaillo Rock Shelter, which is still under study, the same strategy has been followed as at the previous site, recording a total of 26,079 objects. Interventions have only been carried out when necessary. The general state of preservation of the extracted bones is good, which has made it possible to restrict direct intervention to 256 fossils (2% of the total; Figure 27). We can highlight that these actions are often associated with accumulations of bones in certain isolated areas of the site. Additionally, a new methodology has been applied, which consists of the application of an adhesive layer onto the surfaces instead of placing a gauze covering. The results have been optimal as we have prevented the disintegration of the fragments that make up a bone, while they were forced to remain at the site and, at the same time, spatial archaeological and taphonomic studies have been conducted.

Finally, Buena Pinta Cave, like Navalmaillo Rock Shelter, continues to be studied and by 2014, it has the lowest intervention ratio of the three sites, counting just 84 of 1856 fossils (0.3%; Figure 28). The good state of preservation of these bone fossils and the scarce number of complete bones has required direct action only on very few occasions.



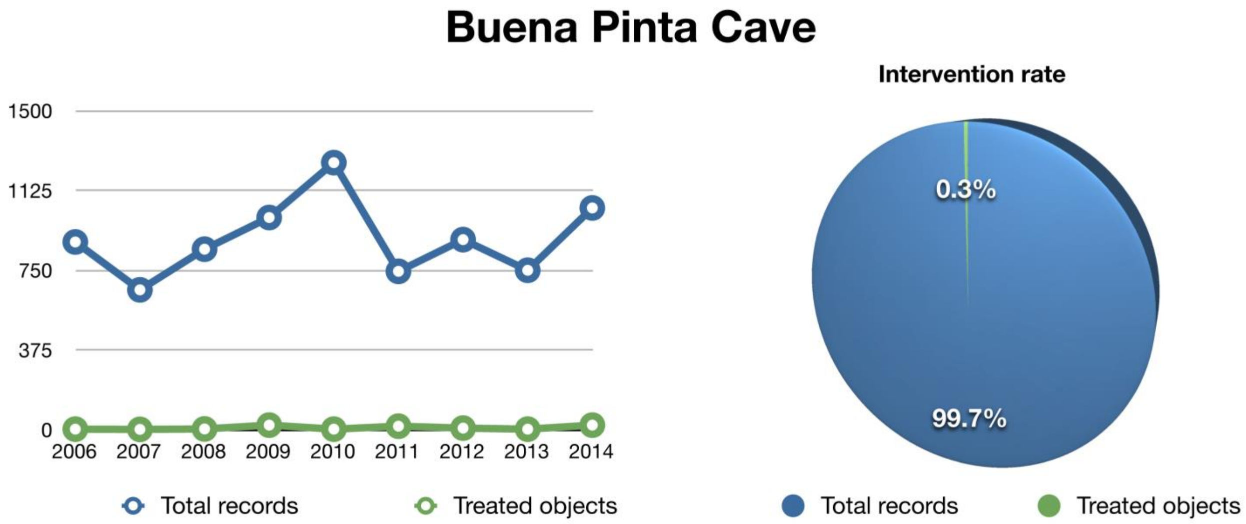
	Total records	Treated objects
2006	765	75
2007	510	7
2008	359	6
2009	222	22

Figure 26 - Camino Cave, total of recovered objects vs. treated objects from 2006 until 2009.



	Total records	Treated objects
2006	2598	51
2007	3291	11
2008	4625	10
2009	4510	28
2010	1425	12
2011	2163	15
2012	1350	26
2013	2778	86
2014	3339	17

Figure 27 - Navalmaíllo Rock Shelter. Total of recovered objects vs. objects that received treatment from 2006 until 2014.



	Total records	Treated objects
2006	883	3
2007	658	2
2008	849	4
2009	998	22
2010	1256	3
2011	745	17
2012	894	8
2013	750	3
2014	1043	22

Figure 28 - Buena Pinta Cave, total of recovered records and objects that received interventions from 2006 until 2014.

The method of preventive conservation can be very efficient. In the long term, we are attempting to integrate it into a comprehensive risk management plan for the sites. The premise of "anticipating the damage" or prevention requires an initial investment of time and resources, carrying out an exhaustive analysis of the sites that results in long-term conservation strategies. Risk management is being applied to collections, urban landscapes and archaeological excavations in different countries (Kamermans et al., 2009; Michalski & Pedersoli, 2009; Reinar & Westerlind, 2010; Cohen & Fernández Reguera, 2013; Antomarchi et al., 2014), with Petra (Jordan) being perhaps the most significant to date (Cesaro et al., 2012; Paolini et al., 2012). The combination of these methodologies in the Pinilla del Valle sites positively influences both the long-term preservation of the environment as well as the creation of synergies among all members of the technical team.

Since this is an excavation in which experts and many volunteers participate, important education and training is directed at all those students, who wish to collaborate with the conservation technicians. One of the responsibilities of the excavation team includes disseminating the results to the society. The results from each excavation season are presented to the general public and to the press through a selection of materials.

CONCLUSIONS

The study of the state of conservation of the materials from the Pinilla del Valle sites has allowed us to gain an understanding of fossil-specific issues, depending on the use or function of each site during the Pleistocene and the concrete post-depositional processes in the different sites.

Fossil state of preservation and extent of decay vary, depending on whether it was a space occupied by carnivores or by humans, specifically by Neanderthals as was the case here, since each group manipulates bones differently. Another relevant factor that must be taken into account is the type of bone, and if it is complete or fragmented. On the other hand, we must consider whether these fragments are fractured by animals or humans, if the breakage has been produced by collapses, by geological agents or by external agents, etc. In this regard, the specialized training of conservators, as well as knowledge in excavation and fossil analysis, is essential for the assessment of which treatments are necessary to be carried out, in addition to the correct methodology of recovery of the objects and the information they provide.

Understanding fossil morphology is of key importance, because knowledge of the anatomy is the best guide for the proper recovery of the bones. Likewise, we must be aware that these objects will be published in scientific literature, which is why it is important to keep in mind all aspects of the fossil: surfaces, raw material, length, etc. (López-Polín, 2012).

From the aspect of object treatment, ensuring the stability of the fossils has taken precedence, which prevents greater decay and allows for a complete interpretation of the object as a whole. Here, we highlight the importance of exchanging opinions, keeping in mind the needs of each professional involved for the purpose of scientific research. The ultimate goal is to gain a better understanding of the Neanderthal way of life and habits, as well as of the characteristics of their environment.

The present study seeks to provide a contribution to all professionals who work with paleontological material in terms of providing a protocol of the methodologies applied to the preservation and conservation of fossil specimens starting from the moment they are excavated until they are stored at the research center (Ortega et al., 2009). We emphasize the importance of working with a trained professional in this field within an inter-disciplinary scientific team.

ACKNOWLEDGMENTS

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REFERENCES CITED

AIC. 1994. Code of Ethics and Guidelines for Practice. The American Institute for Conservation of Historic & Artistic Works, Washington, DC, USA, 10 pp.

Alférez, F., and B. Roldán Garrido. 1992. Un molar humano anteneandertal con patología traumática procedente del yacimiento cuaternario de Pinilla del Valle (Madrid). Munibe (Antropología-Arqueología) Suppl. 8:183–188.

Alférez, F., G. Molero, and E. Maldonado. 1985. Estudio preliminar del úrsido del yacimiento del Cuaternario medio de Pinilla del Valle (Madrid). Coloquios de Paleontología 40:59–67.

Alférez, F., G. Molero, E. Maldonado, V. Bustos, P. Brea, and A. M. Buitrago. 1982. Descubrimiento del primer yacimiento cuaternario (Riss-Würm) de vertebrados con restos humanos en la provincia de Madrid (Pinilla del Valle). Coloquios de Paleontología 37:15–32.

Antomarchi, C., A. Brokerhof, and J. Stevenson. 2014. Reducing risks to cultural heritage: Analysis of a course metamorphosis. Education and Training in Conservation:1–8.

Arriaza, M. C., R. Huguet, C. Laplana, A. Pérez-González, B. Márquez, J. L. Arsuaga, and E. Baquedano. In press. Lagomorph predation represented in a middle Palaeolithic level of the Navalmaíllo Rock Shelter site (Pinilla del Valle, Spain), as inferred via a new use of classical taphonomic criteria. Quaternary International.

Arsuaga, J. L., E. Baquedano, A. Pérez-González, N. Sala-Burgos, N. García García, D. J. Álvarez Lao, C. Laplana Conesa, R. Huguet Pàmies, P. Sevilla, E. Maldonado, H.-A. Blain, R. M. Quam, M. B. Ruiz-Zapata, P. Salas, M. J. Gil-García, P. Uzquiano Ollero, and A. Pantoja. 2010. El yacimiento arqueopaleontológico del Pleistoceno Superior de la Cueva del Camino en el Calvero de la Higuera (Pinilla del Valle, Madrid). Zona arqueológica 422–442.

Arsuaga, J. L., E. Baquedano, and A. Pérez González. 2011. Neanderthal and carnivore occupations in Pinilla del Valle sites (Community of Madrid, Spain); pp. 111–119 in L. Oosterbeek and C. Fidalgo (eds.), Proceedings of the XV World Congress of the International Union for Prehistoric and Protohistoric Sciences. British Archaeological Reports International Series. Archaeopress, Oxford, UK.

Arsuaga, J. L., E. Baquedano, A. Pérez-González, N. Sala, R. M. Quam, L. Rodríguez, R. García, N. García, D. J. Álvarez-Lao, C. Laplana, R. Huguet, P. Sevilla, E. Maldonado, H.-A. Blain, M. B. Ruiz-Zapata, P. Sala, M. J. Gil-García, P. Uzquiano, A. Pantoja, and B. Márquez. 2012. Understanding the ancient habitats of the last-interglacial (late MIS 5) Neanderthals of central Iberia: Paleoenvironmental and taphonomic evidence from the Cueva del Camino (Spain) site. Quaternary International 275:55–75.

Baquedano, E., B. Márquez, C. Laplana Conesa, J. L. Arsuaga, and A. Pérez-González. 2014. The archaeological sites at Pinilla del Valle (Madrid, Spain); pp. 577–584 in R. Sala Ramos (ed.), Pleistocene and Holocene hunter-gatherers in Iberia and the Gibraltar Strait: the current archaeological record. Burgos, Spain.

Baquedano, E., B. Márquez Mora, A. Pérez-González, M. Mosquera Martínez, R. Huguet Pàmies, J. A. Espinosa, L. Sánchez-Romero, J. Panera Gallego, and J. L. Arsuaga. 2011. Neandertales en el valle del Lozoya: los yacimientos paleolíticos del Calvero de la Higuera (Pinilla del Valle, Madrid) Valle del Lozoya: los yacimientos paleolíticos del Calvero de la Higuera (Pinilla del Valle, Madrid). Mainake 33:83–100.

Baquedano, E., J. L. Arsuaga, and A. Pérez-González. 2010. Homínidos y carnívoros: competencia en un mismo nicho ecológico pleistoceno: los yacimientos del Calvero de la Higuera en Pinilla del Valle. Actas de Las Quintas Jornadas de Patrimonio Arqueológico En La Comunidad de Madrid 61–72.

Cesaro, G., M. S. Quintero, A. Paolini, P. J. D. Vos, E. Glekas, and L. Visconti. 2012. Preliminary risk assessment at the Petra Archaeological Park recording strategy. International Journal of Heritage in the Digital Era 1:295–312.

Cohen, D., and M. O. Fernández Reguera. 2013. Valoración de Colecciones. Una Herramienta Para La Gestión de Riesgos En Museos. Museo Nacional de Colombia, Bogotá, Columbia, 32 pp.

Davidson, A., and S. Alderson. 2009. An introduction to solution and reaction adhesives for fossil preparation. Methods In Fossil Preparation: Proceedings of the First Annual Fossil Preparation and Collections Symposium 53–62.

Davidson, A., and G. W. Brown. 2012. ParaloidTM B-72: practical tips for the vertebrate fossil preparatory. Collection Forum 26:99–119.

Down, J. L., M. A. MacDonald, J. Tetreault, and R. Scott Williams. 1996. Pruebas de adhesivos en el Canadian Conservation Institute-una evaluación de una selección de adhesivos acrílicos y de acetato de polivinilo. Cuadernos Sobre Conservación 41:12–21.

ECCO. 2003. E.C.C.O. Professional Guidelines (II). European Confederation of Conservator-Restorers' Organisations A.I.S.B.L., Brussels, Belgium, 4 pp.

Huguet Pàmies, R., J. L. Arsuaga, A. Pérez-González, M. C. Arriaza, M. T. N. Sala Burgos, C. Laplana Conesa, P. Sevilla, N. García García, D. Álvarez Lao, H. A. Blain, and E. Baquedano. 2010. Homínidos y hienas en el Calvero de la Higuera (Pinilla del Valle, Madrid) durante el Pleistoceno superior. Resultados preliminares. Zona arqueológica 13:445–458.

ICOM-CC. 1984. The conservator-restorer: a definition of the profession. 7th Triennal Conference.

ICOM-CC. 2008. Terminology to characterize the conservation of tangible cultural heritage. 15th Triennal Conference 1–2.

Johnson, J. S. 1994. Consolidation of archaeological bone: a conservation perspective. Journal of Field Archaeology 21:221–233.

Kamermans, H., M. van Leusen, and P. Verhagen. 2009. Archaeological Prediction and Risk Management. Leiden University Press, Leiden, Netherlands, 162 pp.

Koob, S. P. 1986. The use of Paraloid B-72 as an adhesive: its application for archaeological ceramics and other materials. Studies in Conservation 31:7–14.

Kres, L. A., and N. C. Lovell. 1995. A comparison of consolidants for archaeological bone. Journal of Field Archaeology 22:508–515.

Laplana, C., P. Sevilla, H.-A. Blain, M. C. Arriaza, J. L. Arsuaga, A. Pérez-González, and E. Baquedano. 2016. Cold-climate rodent indicators for the Late Pleistocene of Central Iberia: New data from the Buena Pinta Cave (Pinilla del Valle, Madrid Region, Spain). Comptes Rendus Palevol 15:696–706.

López-Polín, L. 2012. Possible interferences of some conservation treatments with subsequent studies on fossil bones: A conservator's overview. Quaternary International 275:120–127.

Márquez, B., E. Baquedano, A. Pérez-González, and J. L. Arsuaga. In Press. Microwear analysis of Mousterian quartz tools from the Navalmaíllo Rock Shelter (Pinilla del Valle, Madrid, Spain). Quaternary International 1–14.

Márquez, B., M. Mosquera, E. Baquedano, A. Pérez-González, J. Panera, J. A. Espinosa, J. L. Arsuaga, and J. Gómez. 2013. Evidence of a neanderthal-made quartz-based technology at Navalmaíllo Rockshelter (Pinilla del Valle, Madrid region, Spain). Journal of Anthropological Research 69:373–395.

Michalski, S., and Z. L. Pedersoli. 2009. Manual de Gestión de Riesgo En Colecciones. UNESCO, Paris, France, 97 pp.

Ortega, M. C., A. Gracia, J. M. Carretero, I. Martínez, R. Quam, and J. L. Arsuaga. 2009. Restauration d'un fémur fossile humain du site de la Sima de los Huesos (Atapuerca, Espagne). L'Anthropologie 113:233–244.

Paolini, A., A. Vafadari, G. Cesaro, M. S. Quintero, K. Van Balen, and O. Vileikis. 2012. Risk Management at Heritage Sites: A Case Study of the Petra World Heritage Site. UNESCO, Paris, France, 172 pp.

Pérez-González, A., T. Karampaglidis, J. L. Arsuaga, E. Baquedano, S. Bárez, J. J. Gómez, J. Panera Gallego, B. Márquez Mora, C. Laplana Conesa, M. Mosquera Martínez, R. Huguet Pàmies, P. Salas, M. C. Arriaza, A. Benito, E. Aracil Ávila, and E. Maldonado. 2010. Aproximación geomorfológica a los yacimientos del Pleistoceno Superior del Calvero de la Higuera en el Valle Alto del Lozoya (Sistema Central Español, Madrid). Zona arqueológica 404–420.

Pastor Pérez, A., and O. Canseco Domínguez. In Press. Hacia la auto-sostenibilidad en procesos de excavación: conservación preventiva y gestión de riesgos. Actas Del CotArq.

Reinar, D. A., and A. M. Westerlind. 2010. Urban Heritage Analysis. A Handbook about DIVE. Riksantikvaren, Oslo, Norway, 42 pp.

Storch, P. S. 1983. Field and laboratory methods for handling osseous materials. Conservation Notes 1–4.

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TREATING A HISTORIC RESTORATION OF A *MEGATHERIUM* SP. TAIL FROM THE RODRIGO BOTET COLLECTION IN THE MUSEUM OF NATURAL SCIENCES OF VALENCIA

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ABSTRACT

This paper describes the conservation treatment of the fossil remnants of fifteen connected caudal vertebrae from a large *Megatherium* sp. These remnants had already been treated at the beginning of the 20th century, when important additions were added that hid the original bones. The different vertebrae had been mounted over a metal bar that went through metal plates, which were inserted in the neural arches; they had been fixed with plaster and other types of glue. Cracks had appeared along the whole structure in each of the pieces and, most often, they presented the same pattern. The radiological analysis proved that fractures had been caused by the oxidation of the metallic elements that had been inserted during the previous treatment. With our intervention we have stabilized the fossil material, rediscovered the historical reinstatements by eliminating invasive procedures, and maintained the historic mounting by introducing small changes that improve the conservation of the specimen. With all that we have achieved a balance between the historical, scientific and educational dimensions of the specimen.

Keywords: *Megatherium*; deterioration; radiology; fossil restoration

RESUMO [in Portuguese]

A intervenção realizada no inicio do século XX de 15 vértebras caudais em conexão pertencente a um grande megatério, apresentava uma montagem de importantes reintegrações que se sobrepunham e escondiam ao osso original. As diferentes vértebras estão montadas sobre uma barra de metal que passa através de seus arcos neurais, a maioria deles modificados com umas placas metálicas inseridas e sujeitas com gesso Observou-se que cada um dos elementos apresentava um sistema de fraturas, geralmente com o mesmo padrão ao longo da sua estrutura. A análise radiológica mostrou que as fraturas haviam ocorrido por causa de elementos metálicos inseridos no interior dos processos espinhosos, que afetavam e ocasionalmente o corpo vertebral, o que favoreceu o avanço da deterioração. Com a nossa intervenção temos estabilizado o material fóssil, temos redescoberto as reintegrações históricas eliminando intervenções invasivas, e temos mantido a montagem histórica introduzindo pequenas variações que melhoram a conservação do exemplar. Deste modo, temos chegado num equilibro entre a dimensão histórica, científica e didática do exemplar.

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INTRODUCTION AND ANTECEDENTS

The Paleontological Collection Rodrigo Botet is, probably, the most important collection of South American mammal fossils in Europe. Its importance lies in its containing fossils of extinct animals that Darwin found in his famous voyage aboard the "Beagle", which were fundamental in the development of his theory of evolution (Belinchón et al., 2009).

The collection was brought to Valencia from Argentina at the end of the XIX century, and after many difficulties it was finally placed in the Almudín, a historical building in Valencia, Spain, where the Paleontological Museum was installed at that time. Among the valuable items that it contained, besides an almost complete specimen of *Megatherium*, was a tail of *Megatherium* sp., formed by 15 caudal vertebrae in anatomic connection. At the beginning of the 20th century, this tail had been mimetically reconstructed with plaster and mounted on a metallic structure, anchored to a wooden table, which kept the whole group erected thanks to a brace (Figure 1).

At the end of the 1980's, the Almudín was declared unsafe and the paleontological collection had to be moved to a new location, the Valencia's City Council's Exhibit Hall. Thanks to testimonies of the museum workers, we know that the emergency transportation of such specimen required an acrylic resin (the product and the quantity applied on the tail was not known, and the intervertebral spaces were later protected with cellulose packets since the vertebrae were not disassembled for their relocation (Figure 2).

The tail remained in storage until 1993, when it was exhibited to the public for the "Rodrigo Botet and the science world between the two Republics" exhibition. For this occasion, the specimen was placed on a metallic base with a grid shape which permitted the removal of the former strip (or brace) that held the structure (Figure 3). The piece was exhibited there until it was relocated to the American Quaternarian Room in the Natural Science Museum in 1999 (Figure 4). For this last showing, which was the only intervention carried out on the specimen that was properly documented; a conservation treatment action was carried on. It consisted on a consolidation intervention with the acrylic resin Paraloid® B72 dissolved in xylene. The smaller pieces were joined with a cyanoacrylate adhesive, and all gaps were chromatically reintegrated with water-based paint to differentiate real bone from artificial replacements (Salinas Jacques, 2001: p. 395; Figure 5).

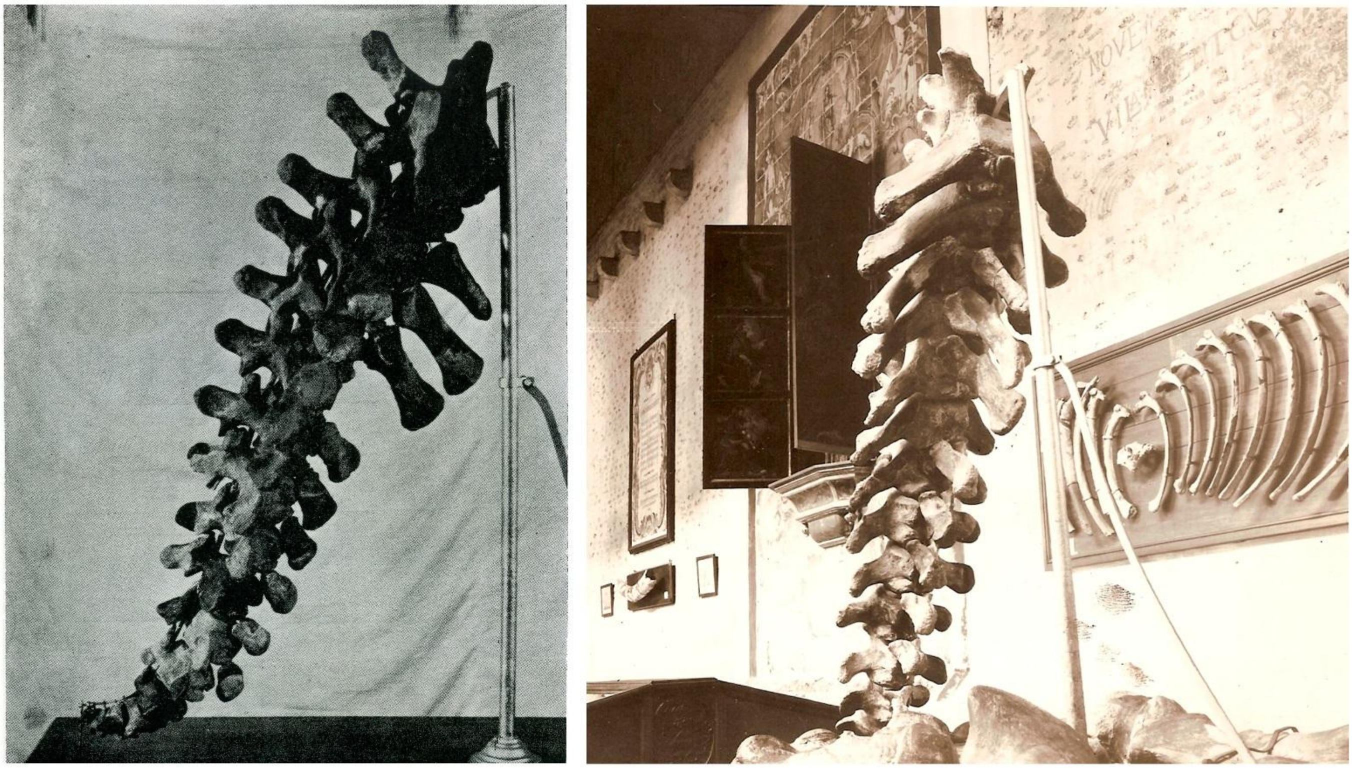

Figure 1 - Historical photographs taken in 1964 that shows the original state of the *Megatherium*'s tail.

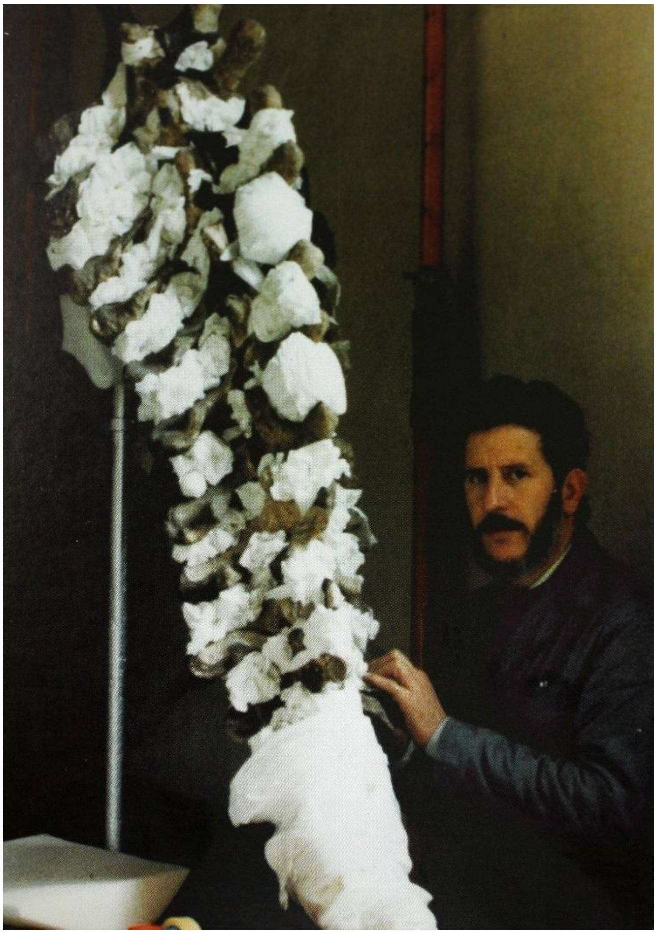

Figure 2 – *Megatherium*'s tail in the emergency transportation from the Almudín to the City Council.

Figure 3 – *Megatherium*'s tail in the exhibition "Rodrigo Botet and the science world between the two republics" in 1993.

Figure 4 - American Quaternarian room in the Natural Science Museum in 1999.

Figure 5 - *Megatherium*'s tail preservation state in 2015, before our intervention. The tail after the 1999 intervention.

AIM OF WORK

At the end of 2014, the Museum of Natural Science was requested the loan of three emblematic specimens for the collection Rodrigo Botet, including the specimen that is the subject of this paper, to be part of the temporary exhibit "Se fueron con el viento: la sexta extinción" ("Gone with the wind: the sixth extinction"), in the Museo de la Evolución Humana de Burgos (Museum of Human Evolution in Burgos).

For that event, our main objective was to ensure stability in the vertebral set for it to be moved. Therefore, the parts were to be studied and prepared so as not to suffer any damage during handling. We treated this specimen by giving priority to current tendencies and criteria in restoration. Consequently, we tried to uncover the historical interventions from the beginning of the 20th century that had been hidden by the layer of paint applied in 1999.

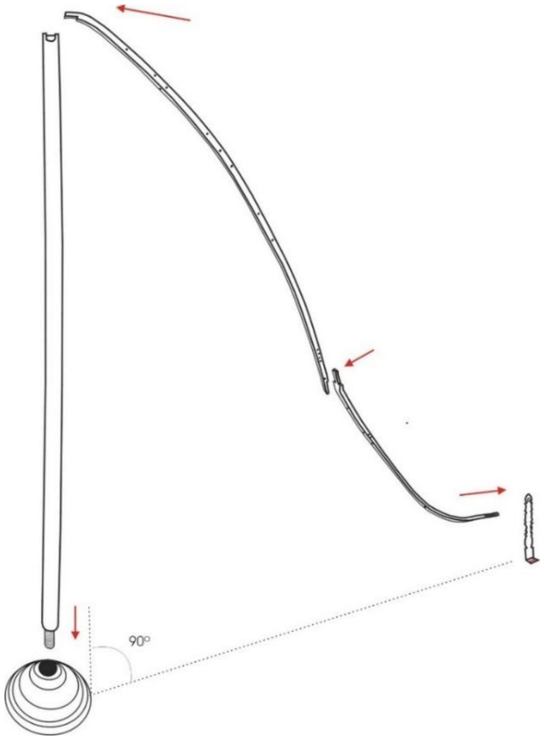

Figure 6 - Diagram of the assembly's internal structure.

With this intervention, we tried to preserve and reveal the historical, didactic, and scientific character of the specimen.

DIAGNOSTIC ANALYSIS AND PRESERVATION STATE

Organoleptic study

The vertebrae were mounted on a metallic structure consisting of a vertical rod where a metal bar, consisting of two sections which were joined by a screw, was secured (Figure 6). This metal bar had transverse perforations in which metal elements of different shapes were inserted and were used to hold the vertebrae (both ends were held to the metallic rack on the base with bolts and nuts). The vertebrae were held by a bar that goes through the neural arches with several metallic elements inserted into the holes of said bar (Figure 7). Besides, only five metallic elements hold the fifteen vertebrae (Figure 8). They were interspersed in the bar's length, so that five vertebrae were actually fixed to the bar preventing the other ones from moving. Some vertebrae were also exerting pressure against the others, as a consequence of the assembly system onto the metallic structure (Figure 9).

The bar consisted of two parts in two halves (perhaps for ease of assembly): very likely, the most proximal vertebrae were inserted first, then the second section of the bar was screwed and the rest of the vertebrae were inserted. In addition, natural cork discs were used as a cushioning layer between each vertebra (Figure 10).

In the vertebrae, the neural canals were found to have been modified: the proximal vertebrae

Figure 7 - Limit or metallic brake to hold the vertebrae.

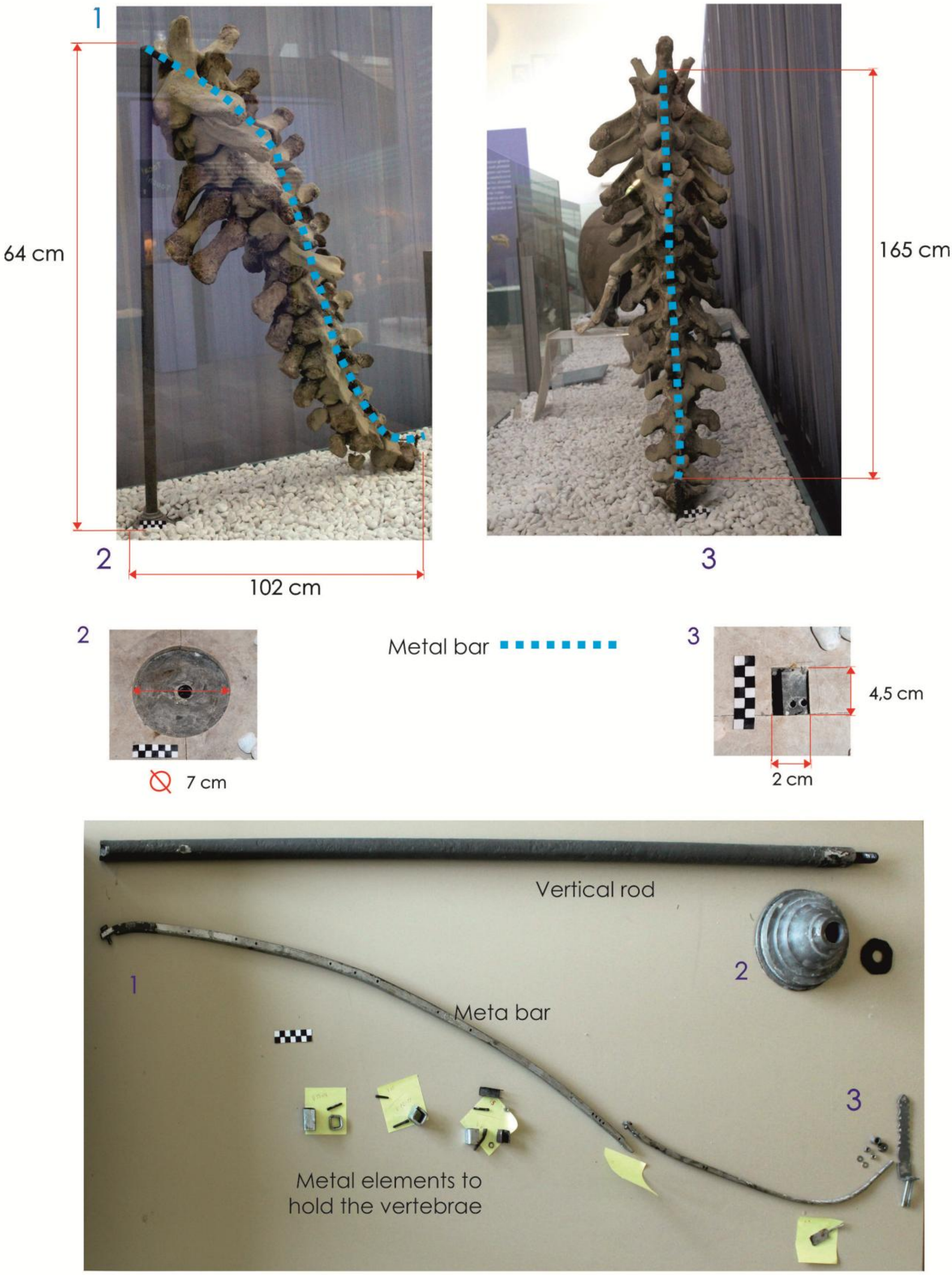

Figure 8 - Breakdown of the *Megatherium*'s tail mounting.

Figure 9 - "Squashing" effect of the vertebrae due to the assembly structure.

Figure 10 - Natural cork discs between vertebrae.

included the insertion of metallic sheets with plaster (Figure 11); the distal ones, however, had their canals sawed in order to make it wider (Figure 12); in other cases eye bolts had been inserted into vertebrae without a neural canal (Figure 13).

The most proximal vertebrae (vertebrae 1 to 7) had their neural canals altered with corroded metal sheets inserted into them. The iron oxide had moved into the bone and the historical reintegrations. The most distal vertebrae (vertebrae 7 to 11) that had the neural canal drilled had suffered damage due to the metal abrasion over them. The last vertebrae (vertebrae 12 to 15) with metallic elements inserted for the assembly in the metallic structure had cracked around the drilling areas.

We found fragments detached by the alteration of some of the adhesives used in 1999 such as cellulose nitrate (Figure 14), and other adhesives used previously, such as shellac and wax, which remained in a good state (Figure 15).

The 1999 paint layer hid both the historical restoration of the specimen and the large sections of the fossilized bone. This prevented the appropriate observation of the specimen. The plaster filler, or more specifically the way in which it was applied at the beginning of the 20th century, produced a similar confusion concerning the interpretation of the specimen (Figure 16).

The chevrons were hooked to the vertebrae with wires inserted into the osseous matter. Some had been treated with wax filler, and others included marks (like incisions and even drilling) which could be the result of assembling attempts from the original setup (Figure 17).

Natural cork had been used on some spots of the vertebrae and the chevrons, damping the osseous elements of the tail and simulating non fossilized material: in the vertebrae they are placed in the front or rear centers of the

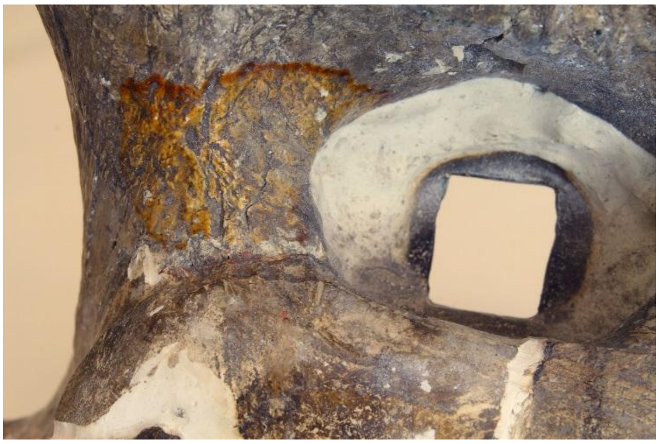

Figure 11 - Application sample of metallic sheets in the neural arch of a proximal vertebra, 6th caudal.

Figure 12 - Canals sawed. Example of a drilled/ perforated canal, 12th caudal vertebra.

Figure 13 - Metallic hook in distal vertebra, 14th caudal vertebra.

Figure 14 - Fragments detached by the alteration of some of the adhesives used in 1999 such as cellulose nitrate, 9th caudal vertebra.

Figure 15 - Wax adhesive. Chevron linked to 10th caudal vertebra.

Figure 16 - Initial condition of the vertebrae after disassembling (12th caudal vertebra).

vertebral bodies, or in both, simulating intervertebral discs (Figure 18); in the chevrons, they are placed over their face joints. Some vertebrae and chevrons showed marks suggesting that some cork elements were used and which have now been lost (Figure 19); while others do not show any trace of having had them.

The cork elements that simulate the intervertebral discs had become brittle and somewhat abrasive on contact. In turn, this produced a loss of material in the bony areas of other vertebrae and in chevrons with which it was in contact. Furthermore, elements of cork that had been lost were causing some vertebrae and some chevrons to touch without any protection, triggering bone material losses.

The metallic elements in the assembling structure, such as the caps of the vertebrae, produced alterations and loss of material in the vertebrae by means of direct contact (Figure 20).

Cracks on the 1999 paint layer and about massive presence of cracks in the osseous tissue were easily visible. More important were the cracks in the vertebrae, which formed a grid pattern (Figures 21, 22).

Radiological study

We can observe a system of cracks in the vertebrae. These appear to open up from the inside. In order to determine the cause of these cracks we carried out a radiological study of the osseous elements in the X-ray laboratory of the Departamento de Conservación y Restauración de la Universidad de Valencia. Through these radiographs we found out that in the inner side of the vertebrae some metal wires and rods were installed to join fragments together, and had filler applied over them. The wires used to hook the chevrons to the vertebrae bore into the osseous matter of the former, opening a system of cracks. The radiographs show that the metallic rods are not sufficiently corroded so as to put its balance in danger. However, the metal and the bone contract and expand at different rates, which produces a weakening of the osseous material due to stress in its internal structure. In addition, it was observed that under the plaster filler there was bone matter, although we did not know its actual condition (Figure 23).

INTERVENTION PROPOSAL AND CRITERIA TO BE FOLLOWED

The *Megatherium*'s tail preserved in the Museo de Ciencias Naturales de Valencia (Natural Science Museum of Valencia) was assembled around 1902 according to the principles and methods at the time. As it can be read in a report from 1903 (Boscá y Casanovas, 1903): "it must be noticed that in the restoration of the different pieces of the skeleton, two different procedures were executed. In one of them, filler and cork were used with great care, attempting to conceal the artificial parts". This made reference to the usual reconstructions of that

Figure 17 - Drilled chevron linked to 7th caudal vertebra.

Figure 18 - Natural cork simulating non fossilized material, 2nd caudal vertebra.

Figure 19 - Vertebrae which have now lost the cork elements, 7th caudal front view and rear view.

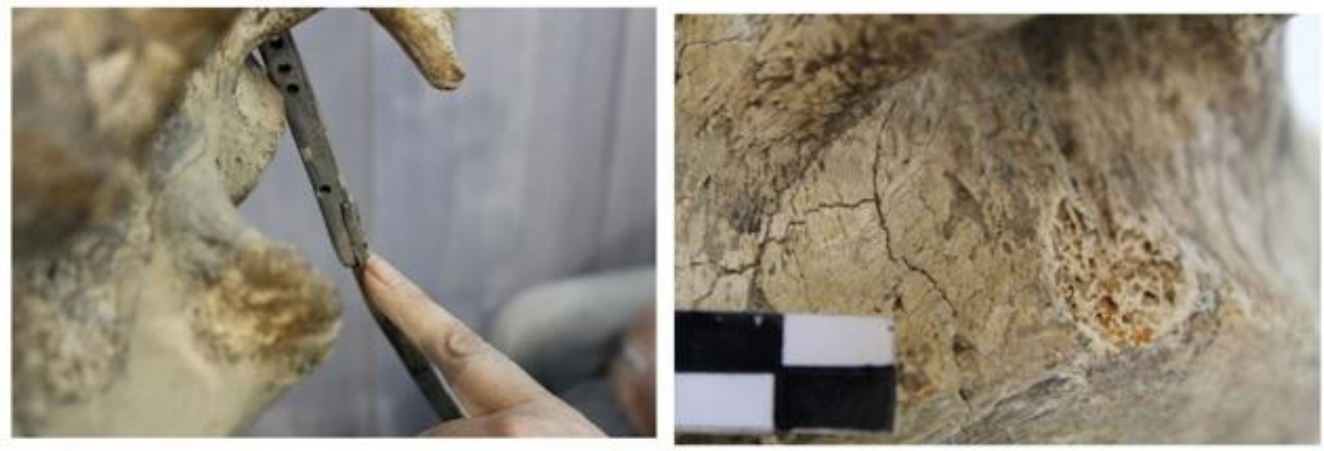

Figure 20 - Loss of material due to direct contact with the metallic bar in the assembly structure in 8th caudal vertebra.

time in museums all over the world. At that time, as the author explains, they tried to join the artificial fragments with the original ones in such a way that the former ones were undistinguishable by even the most expert observers. It was also common to use framing systems that would keep the ensembles erected in an anatomical position. This usually involved the drilling of the bones so that they could be reinforced by metal or wooden rods.

These reinforcements accelerated their deterioration over time. However, the old interventions were somewhat effective in the case of our specimen, since today, after more than a century later, we can still see it as it was assembled in 1903: without having lost any essential part. Because of this, besides its being a fossil specimen of great scientific importance, the piece is also valuable, as it shows the methodologies of different times. It is like

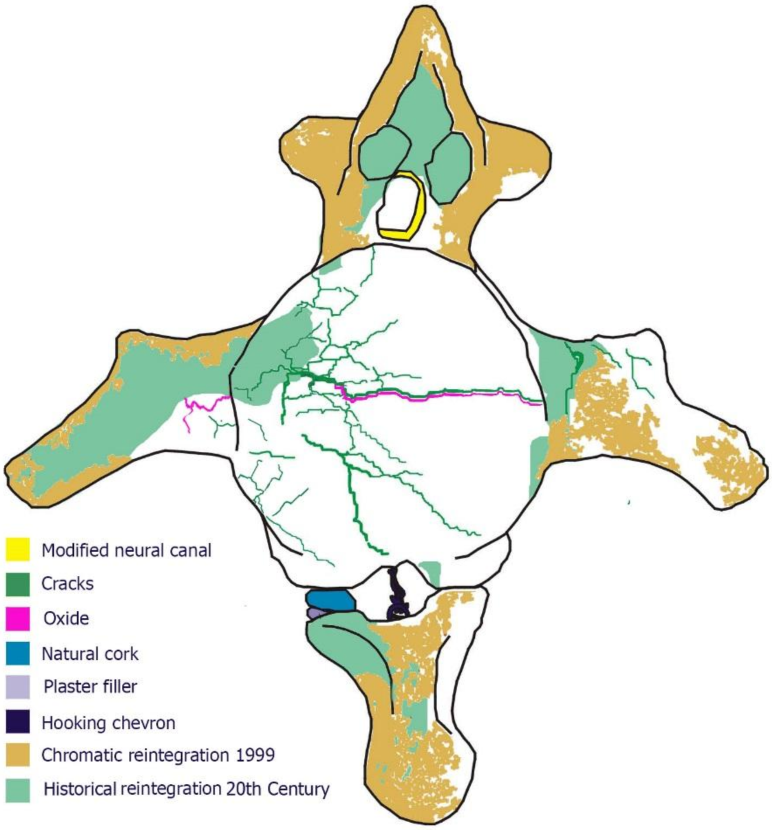

Figure 21 - Mapping of damage, initial condition of the vertebrae after disassembly, 3rd caudal vertebra.

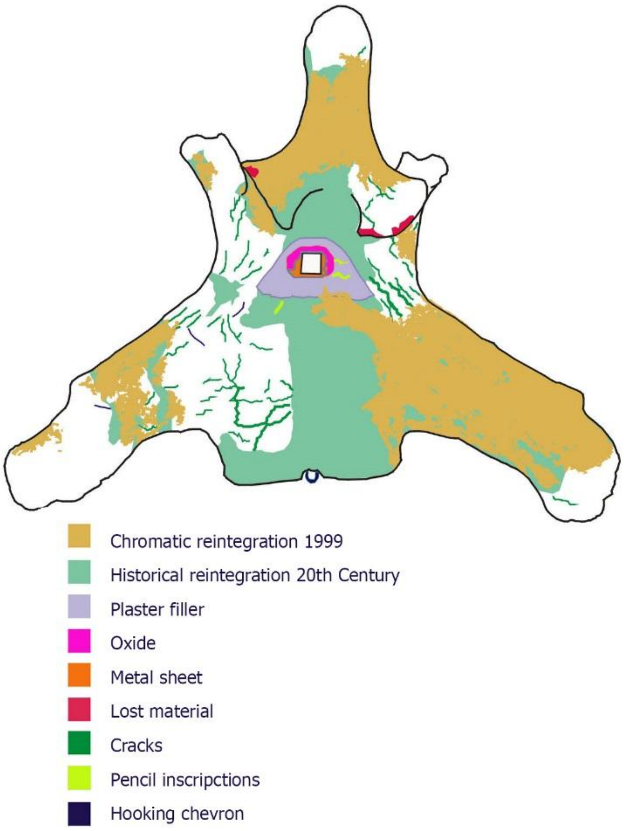

Figure 22 - Mapping of damage, initial condition of the vertebrae after disassembly, 11th caudal vertebra.

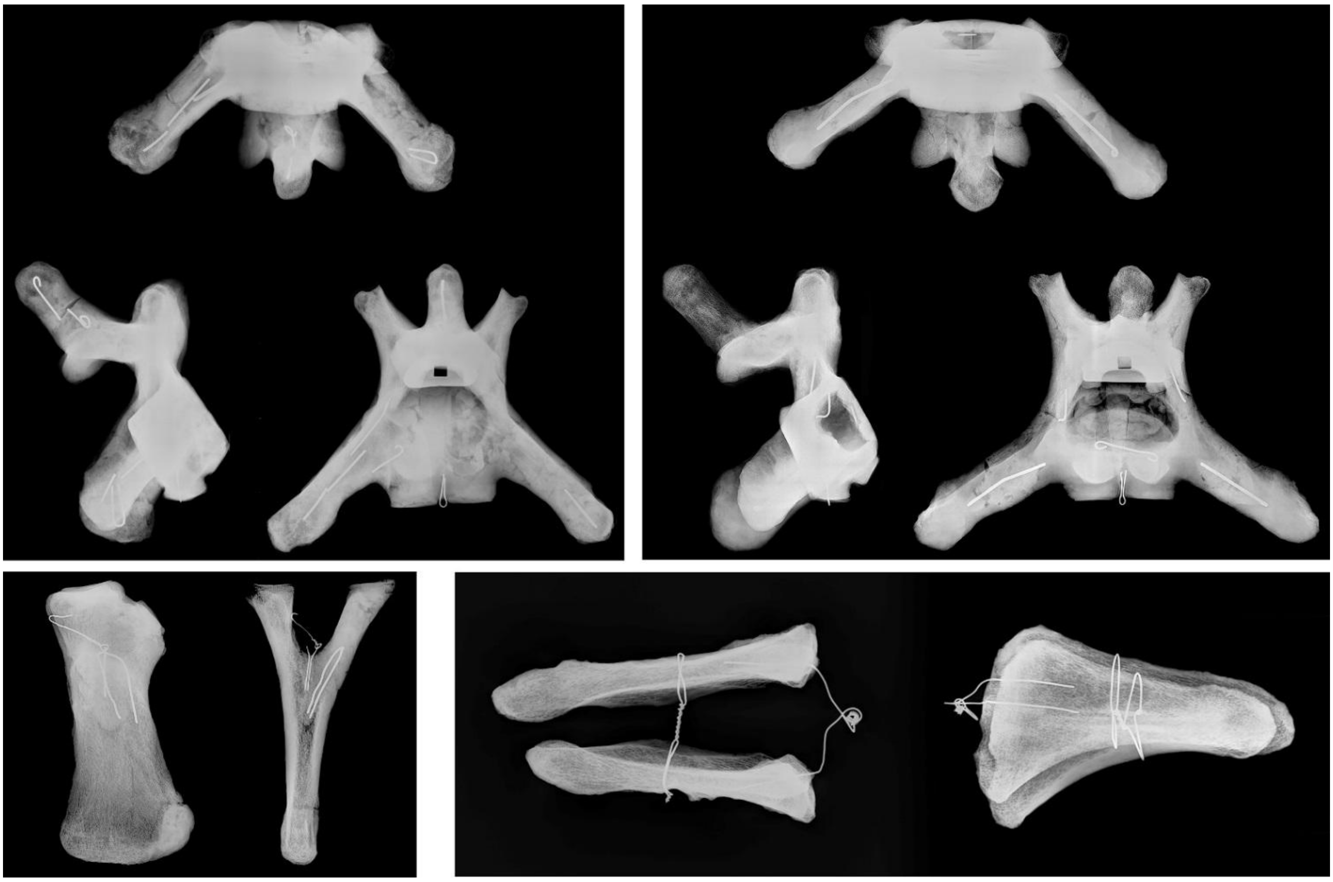

Figure 23 - X-rays. From left to right: 3rd caudal, 2nd caudal, chevron associated to 4th caudal, chevron associated to 2nd caudal.

witnessing a live experiment on the evolution of heritage conservation technique and principles – both of which have become of age as time passes.

Not that long ago, the intervention criteria on specimens did not have much into account the principle of historicity of the object (Brandi, 1977). However, we have considered the implicit values of old restorations, which permit a reflection on the evolution of conservation ethics along the 20th century.

It is of paramount importance to carefully study the specimen in order to make the most appropriate decisions, especially given that, inevitably, some of the operations we could be carrying on were not reversible, despite our trying to avoid irreversibility in every process.

The studies focused on the original historical assembly, on the condition of the specimen and on the materials used in the different conservation treatments. With the results of these studies, we made a more adequate plan for action. We have approached our work trying to respect previous interventions. We consider that the object of this paper is a living testimony of the paleontological and museographic activity from the 19th century.

We accept that the first actions on the specimen would not be acceptable from contemporary ethical standard, as they do not abide by the principles of discernibility and of minimum intervention (Carrascosa Moliner, 2009). It is of great interest for curators of paleontological collections to be able to analyze and study the evolution of materials, and to approach conservation problems with caution, resorting to restoration only when the case makes it necessary.

With the support of previous research works, we assess the state of preservation of the piece, try to foresee its behavior in the future, and make decisions about the most appropriate conservation technique in order to get the maximum potential from the heritage object. But, how can we best do it?

According to Muñoz Viñas (2004: p. 177), "the right restoration is the one that harmonizes, as much as possible, and gathers together the maximum number of approaches. A good restoration is the one that damages the least the smallest number of sensitivities, or the one that is more satisfying for more people. There is not a good restoration, but rather a good restoration of a particular object in a particular circumstance".

Based on this idea, and considering the author's recommendations, we aimed at fulfilling the different needs according to current directives on the intervention of patrimonial goods. This meant bringing the specimen into a new condition in which all its possible values (that "are not discriminatory but complementary"; Muñoz Viñas, 2004: p. 63), and all its functions are preserved as much as possible. It is about bringing together the possible meanings of the fossil (symbolic, didactic and scientific) by means of a dialogue between the old and the new. In order to achieve this historical dialogue, it was decided to take the bone back to its original condition, thus revealing the reconstruction and the assembly marks under the 1999 paint layer, making a discernible difference between the early 20th century intervention and the current one. Previous studies and analysis of the specimen have been decisive in order to plan the intervention and estimate its viability. For that purpose, we disassembled the tail. We made an organoleptic analysis, physical and mechanical cleaning tests, and a radiological study that served to diagnose the specimen's state.

With the results obtained from the previous studies, it was proposed to remove the paint layer from 1999, which hid the historical reintegrations and the original bone.

The plaster filler from 1902 would be partially removed in the places in which it hid the original bone, when such operation did not pose a risk for the piece. This would make it possible for the spectator to discern where the original bone ends and the reconstruction begins. The historical reconstructions would then be kept without changing its texture or color.

Consolidation of the osseous elements would be essential to restore the mechanical resistance of the specimen and to ensure its durability over time.

Mounting on the original media and parts would be maintained. All bracket metals present in the mounting would be cleaned, removing rust and, afterwards, will be protected against corrosion.

The biggest factor of alteration in the group of vertebrae is the insertion of metallic elements and the tension produced by the squashing of some vertebrae against the others. We cannot remove the metal elements from within the vertebrae to assemble its parts because, on the one hand, they are part of its history, and on the other hand, it would rather entail damage to the fossil material than benefits or advantages. Nevertheless, it is possible to modify the assembly in the metallic bar in order to minimize the negative effects by the squashing**,** the direct contact between vertebrae and the pressure on the vertebrae that support another, without altering the original aspect at the end of the restoration. For that purpose, we inserted the caps, covered with silicone in order to minimize any friction, and the natural cork elements were replaced by an inorganic material**.**

Our intervention intends to be a bridge between two shores, the 'real' and the 'added'. This intervention, therefore, leans both on theory and technique, on the tangible and intangible aspects of the object. In a technical sense, it is aimed at studying and physically preserving the specimen; in a theoretical sense, it establishes a connection between many of the historical values that can be part of a restoration and be transmitted through time.

INTERVENTION PROCESS

Disassembly of the vertebrae

Fifteen caudal vertebrae were disassembled, after carefully preparing the room and gathering the tools and materials that would allow its safe dismantling. All the steps given during the disassembly were registered, in order to be able to reassemble it in the same sequence and in the same way keeping its historical configuration, in the future.

Disassembly began from the distal part of the tail: the anchor that held the assembly to the base was removed, the vertebrae were removed one by one, collecting data from their position and their anchorages to the bar, when there were. In the middle of the bar (vertebra 7) the union of the two sections of the bar can be found; they were disunited and the process was carried on until the first vertebra (Figure 24).

Figure 24 - Dismantling process of the tail.

Cleaning and cleaning test

The concealment of the historical imprints lessened the importance of the specimen and its historical and didactic dimensions, so that the first stage of our treatment was the removal of the paint layer. It was confirmed through cleaning tests that the paint applied in 1999 was indeed a highly soluble in water gouache, while the reconstructions in plaster and pigmented in the early twentieth century were soluble in alcohol, but water stable. This greatly facilitated the removal of the 1999 paint without altering the historical reinstatements (Figure 25).

For physical cleaning, unionized water applied locally and gradually with cotton swabs was used. Then, to avoid an excessive moisture supply in a weak fossil and the metal that it houses inside, this cleaning method was carried out in all skeletal elements in phases, respecting drying times to also minimize stress effects.

As a result of the removal of the painting, the historical reintegrations and the areas where the plaster filler covered the bone were rediscovered, being the cause for accentuating the mimicry and preventing from knowing where the reconstruction ends and the fossil begins (Figure 26).

Lineal markings and numerical inscriptions made in blue and red pencils respectively also appeared from the original assembly. It could be determined that the numbers written on the vertebrae corresponded to an assembling order, and not to an anatomical one (Figure 27). It was also clear that the line marks indicated the area in which the metallic rods were inserted into the vertebrae (Figure 28).

In the second phase of cleaning, we removed the plaster filler that hid the bone, with a mechanical dry cleaning. This operation could delicately be performed by using scalpels and an ultrasound system (Figure 29), along with the help of magnifying glasses and pocket microscopes**,** and stopping the cleaning on the point where the filler had a structural or protective function (Figure 30).

Figure 25 - Cleaning and cleaning test, 1st caudal vertebra.

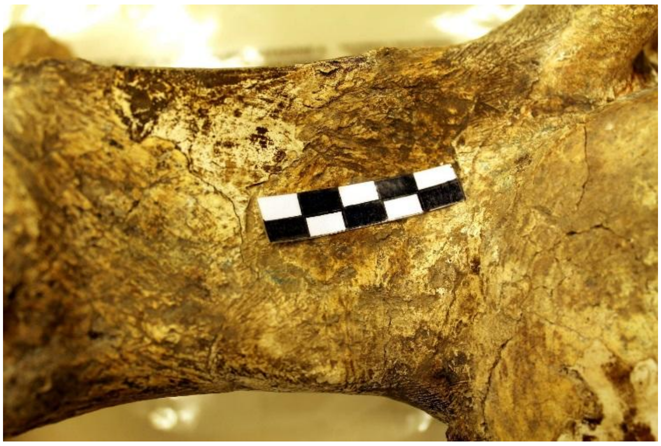

Figure 26 - Detail of historical reintegration in 3rd caudal vertebra.

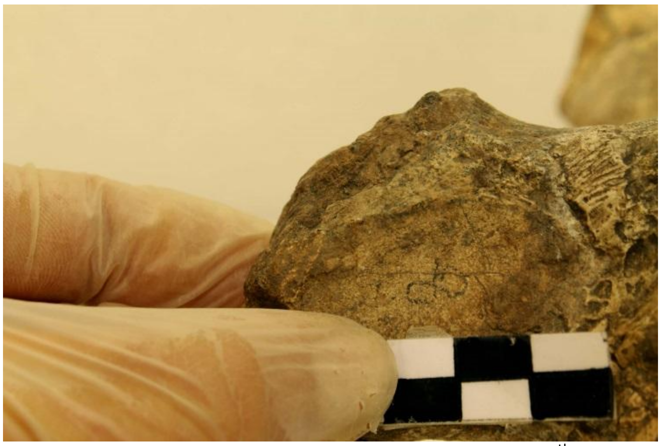

Figure 27 - Pencil numbers. Numerical marks, 8th caudal vertebra.

Figure 28 - Example of lineal pencil marks in chevron linked to 10th caudal vertebra.

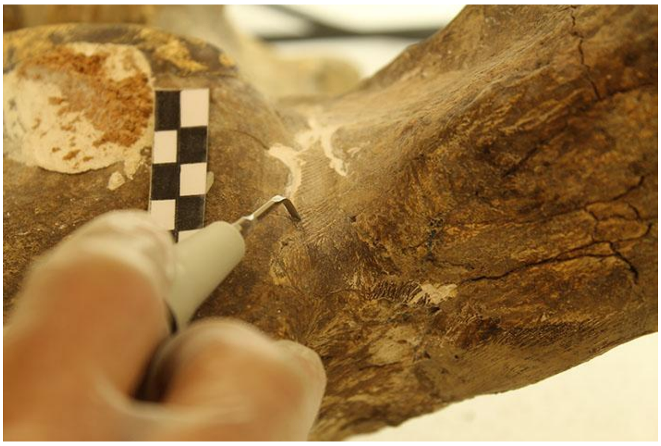

Figure 29 - Boundary process between the fossil bone and the historical reintegration, 5th caudal vertebra.

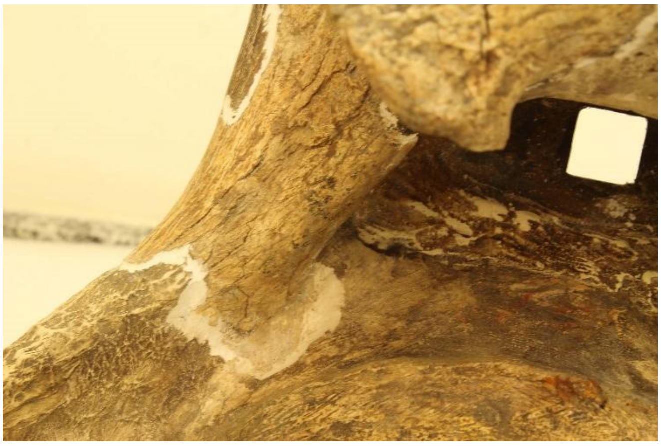

Figure 30 - Vertebrae point where the filler had a structural function, 1st caudal vertebra.

Through this mechanical action, the filler was bevelled and then chromatically reintegrated. Therefore, the shadow of this bevel would allow the perimeter of the original bone to be distinguished from the historical reconstructions. The result of this operation was a subtle mark that allows us to know what part is a modern addition (Figure 31).

Cork elements, which appeared on the vertebrae and chevrons as damping elements, were removed because they did not meet its original function and were causing erosion damage on the fossil material. The removal was mechanically done by using scalpels, locally dampening with water and removing the plaster that kept them attached to the fossil (Figure 32).

Figure 31 - Result of boundary process between the fossil bone and the historical reintegration. 1st caudal vertebra

Corrosion

Regarding the oxide stains that were found on the bones, these were not treated because it would have been dangerous for the preservation of the bone.

The oxide was removed from all the metallic elements found in the specimen by immersing them in a 5% solution in water of acetic acid. Those who could not be submerged by its size or location were treated with the same solution but by Arbocel packages and Japanese paper. Later, a corrosion inhibitor (tannic acid in alcohol) applied with a brush and a protective film of Paraloid B64 (15% in alcohol) was applied with brush.

Consolidation and adhesion

In order to increase the mechanical resistance of the bone, a consolidation treatment was performed in two stages. In the first stage, an ethyl silicate was impregnated on the whole osseous compound. Ethyl silicate is a chemical strengthener that has proved useful in consolidating fossilized bones, because it regenerates the silicon bonds. In the second stage, we applied an acrylic resin (Paraloid® B72 at 20% with acetone) on specific spots where the surface of the bone was more

Figure 32 - Removal of the cork and the plaster which joined the vertebra.

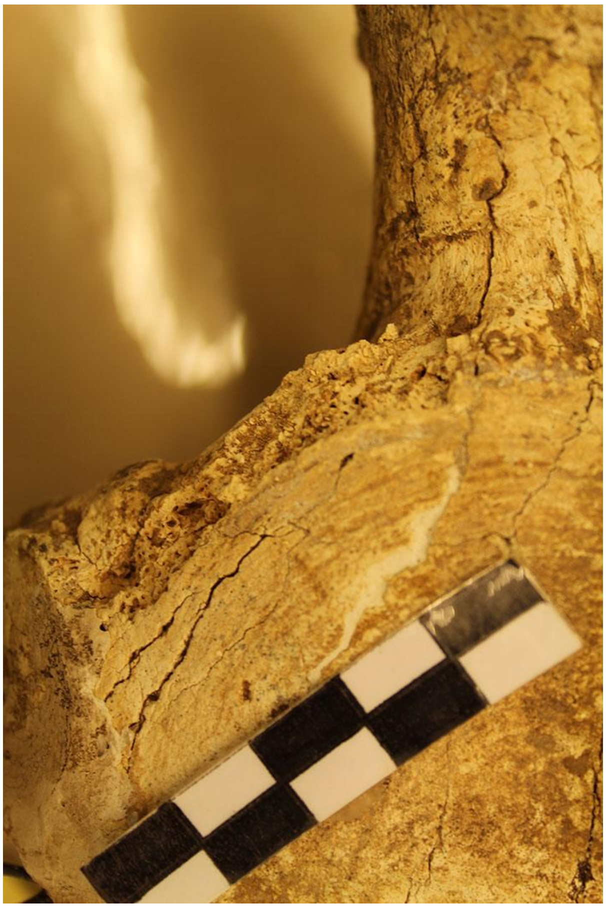

Figure 33 - Example of some specific spots where the surface of the bone was consolidated.

severely damaged, binding together the bone in a dusty state and protecting it from new abrasions (Figure 33).

The detached fragments were joined with an acrylic resin (Paraloid B72 at 50% with acetone) after removing the nitrocellulose adhesive remains using cotton swabs dampened in acetone.

Chromatic and volumetric reintegration

Those areas that had lost material were coated with plaster filler (Figure 34). Then we chromatically reintegrated with water based colour (gouache) the bevels made in the mechanical cleaning stage, and also the filler applied on the areas with missing matter. This was done in order make it possible to discern the fossilized bone from the historical reintegration and the historical reintegration from our intervention (since the last one lacked any texture; Figures 35 and 36).

Figure 34 - Volumetric reintegration with plaster filler.

Figure 35 - Final state of chevron associated to 4th caudal vertebra after the volumetric and chromatic reintegrations

Relocation and assembly

The vertebrae were prepared for its transport and exhibition by wrapping them in conservation paper and blocking them with polyethylene, which protected them from vibrations – as is usually done for transporting fossils.

A platform was built with the appropriate dimensions and resistance. On this platform the *Megatherium*'s tail and its original support were mounted, with the crucial help of the records taken during its disassembly and the experience gained in assembly rehearsals in laboratory. Firstly, the vertical shank of the metal structure was mounted on a wooden base; this shank was joined to the proximal section of the metal bar, through which the more proximal vertebrae go (vertebrae 1-7). Then, the distal section of the metal bar was joined, whereby the remaining vertebrae were inserted (vertebrae 7-15; Figure 37).

Throughout the intervention process, it has been tried to preserve the original assembly, keeping the design, but introducing corrective

Figure 36 - Final state of skeletal elements after the volumetric and chromatic reintegrations. From left to right: 2nd caudal and 7th caudal vertebrae before and after our intervention.

Figure 38 - New limit insertion with a silicone lining.

Figure 37 - Mounting process in the Museo de la Evolución Humana de Burgos (Human Evolution Museum, Burgos).

Figure 39 - Final state of the vertebral compound and exhibit in the Museo de la Evolución Humana de Burgos (Human Evolution Museum, Burgos).

measures to prevent the deterioration of the piece. The only modifications in the assembly were the insertion of new caps and hooks of the vertebrae to the bar, so that each vertebra would withstand its own weight. At the same time, this allowed an appropriate intervertebral separation that would prevent further alterations due to friction, which made the presence of new cork necessary. Furthermore, the bone was insulated from the metallic elements by covering the metal pieces with silicone tubes (Figure 38). Furthermore, silicone tubes were also placed lining the metal bar to isolate the most distal vertebrae, which had no metal plate in its neural arch, from metal (vertebrae 15-9).

In the areas of direct contact between some skeletal elements, as between vertebra-chevron, small sections (strips) of natural skin were temporarily placed (Exposición temporal La Sexta extinción, Burgos) to prevent friction. For its permanent and definitive exhibition at the Museum of Natural Sciences in Valencia, this skin was replaced by silicone. To protect it from visitors, a four-walled display case without a roof was built, which would host the specimen once assembled. The assembled specimen was accompanied by a sculptured replica made of plaster, which derived from an original sculpture of the 19th century (Figure 39). This way, the fossil specimen can be admired by visitors from any point of view by walking around it, while it is protected from manipulations and accidental scratching from people passing nearby. In the same way, the alterations we introduced in the early 20th century assembly are not easily visible, but protect the specimen from the effects of vibrations and the 'squashing' of some vertebrae against the others (Figure 40).

DISCUSSION AND RESULTS

With this journey through time we have also pleasantly witnessed a valuable sample of past paleontological procedures, an intervention once praised and now questioned. This treatment was performed with some goals and motivations, but it nowadays evidences our evolving attitudes towards heritage. Specimens like this are, so to speak, a real-time experiment of the validity of our conservation procedures through time, and we could ask ourselves how our own intervention on the *Megatherium* will be questioned in the future.

During the 20th century, conservation criteria have been changing. It is obvious that a hundred years ago conservators did not have the techniques or materials we nowadays have, nor did they have our long experience. However, in each historical moment there is a general agreement on what to do and how to do it.

In the original assembly, we have observed a systematization of the preparation and assembly works, despite observing a rather random use of the available materials and tools;

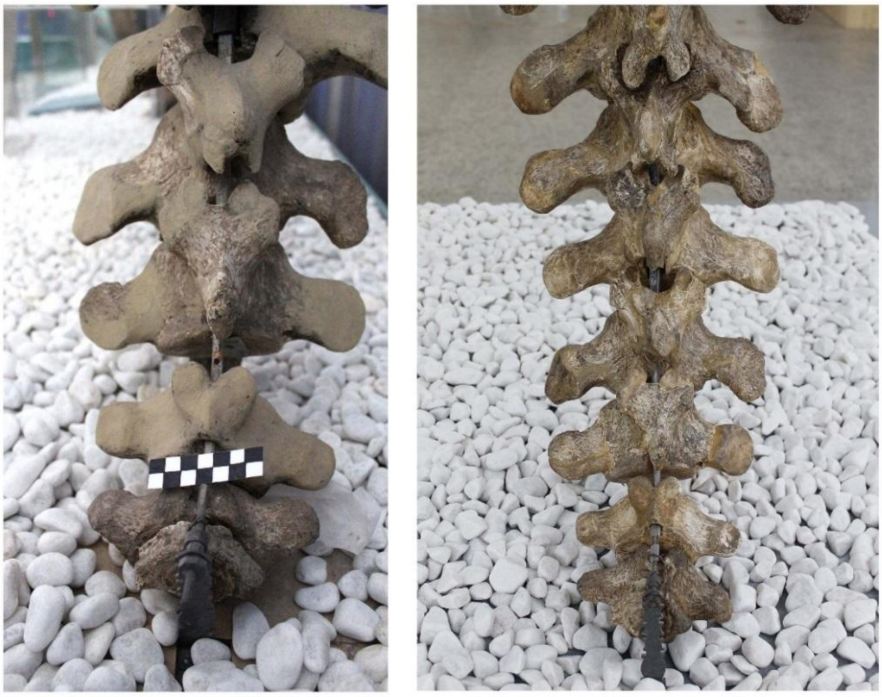

Figure 40 - Detail image showing 'squashing' in some vertebrae against the others before and after our intervention.

Figure 41 - Initial and final state of the *Megatherium's* tail. Rear view.

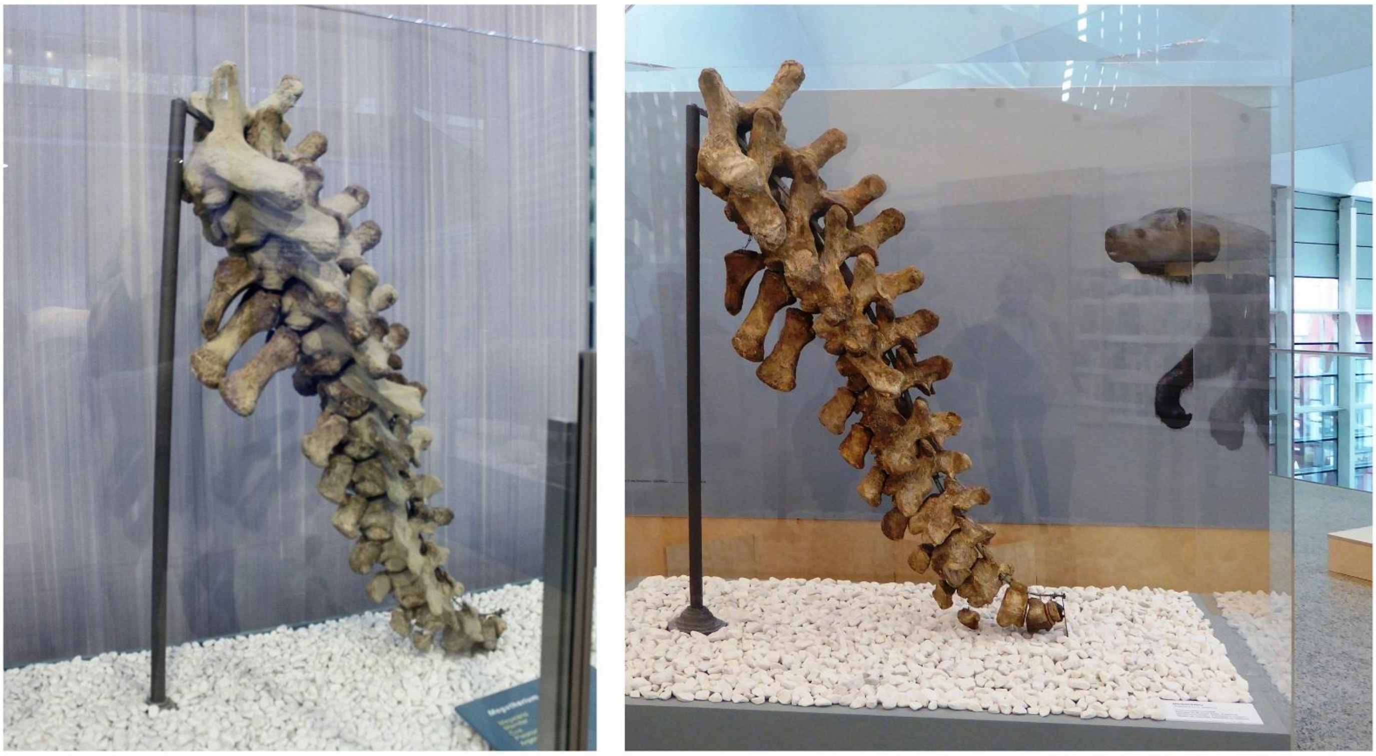

Figure 42 - Initial and final state of the *Megatherium's* tail. Side view.

thus, many of the metal elements that were used as caps to keep the vertebrae fixed to the structure were different from each other, and in some cases the osseous elements were drilled for no apparent reason. However, all fifteen caudal vertebrae of a *Megatherium*'s tail have survived to our days, although drilled, with bolts inside, and hanging from a metal structure. It is evident that the insertion of rods to hold heavy fragments, which is still in use, is not the stable technique unless helped by other joining or holding devices that counteract these effects.

In the same way, it opens a debate on the use of dense plaster fillings which are heavy when they harden, like the conventional ones based on calcium sulphate, which also weaken the material by means of transmission of salts and other substances. Cases like this encourage us to think of alternative exhibition and reintegration techniques, and push us to think in new techniques or tools to achieve methods that are reversible and fully harmless to the fossil. We must bear in mind that our intervention is done following some criteria, but will surely be judged with different criteria. Paradoxically, this change of criteria may mean an improvement as well as a pathology. We cannot forget the danger of deterioration of all those specimens that are almost forgotten in our collections, without considering what were their preventive conservation measures, maintenance and their eventual restoration.

With this treatment we have achieved the stabilization of the material and the recovery of some historical interventions; we have gathered the scientific and museographic dimensions of the specimen with its historical one. In its present condition, the *Megatherium*'s tail now provides paleontological information, but also provides valuable insight on the conservation techniques at the beginning of the 20th century (Figure 41 and 42).

ACKNOWLEDGMENTS

We are grateful to Mr. José García Madrid, from the X-ray laboratory of the Departamento de Conservación y Restauración de la Universidad Politécnica de Valencia (Department of Conservation and Restoration of the Polytechnic University of Valencia), for the impeccable radiographs he made of all vertebrae, without which this study would not have been possible.

REFERENCES CITED

Belinchón, M., E. Peñalver, and P. Montoya. 2009. Crónicas de Fósiles. Las Colecciones Paleontológicas Del Museo de Ciencias Naturales de Valencia. Ajuntament de Valencia. Concejalía de Cultura, Valencia, Spain, 534 pp.

Boscá y Casanovas, G. 1903. Informe sobre el estado del esqueleto de megaterio del Museo de Ciencias Naturales de Madrid. Boletín de La Sociedad Española de Historia Natural 3:211–225.

Brandi, C. 1977. Teoría de La Restauración. Giulio Einaudi Editore, Torino, Italy, 152 pp.

Carrascosa Moliner, B. 2009. La Conservación Y Restauración de Objetos Cerámicos Arqueológicos. Tecnos, Madrid, Spain, 23 pp.

Muñoz Viñas, S. 2004. Teoría Contemporánea de La Restauración. Editorial Síntesis, Madrid, Spain, 208 pp.

Salinas Jacques, M. A. 2001. Las colecciones paleontológica y conquilógica del museo paleontológico J. Rodrigo Botet de Valencia: Inventario faunístico, importancia científica, museística e histórica. Ph. D. dissertation, Universitat de València, Valencia, Spain, 395 pp.

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PAST PREPARATION PROCEDURES AND CONTEMPORARY CONSERVATION TECHNIQUES APPLIED TO A HOLOTYPE (MUSEO GEOMINERO, MADRID, SPAIN)

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ABSTRACT

The past preparation processes carried out on the holotype of the species *Sinohippus sampelayoi* (Villalta and Crusafont, 1945) (Equidae, Anchitheriinae) have been analyzed. This singular piece, a right hemimandible housed in the Museo Geominero since 1940's decade, has undergone an unusual number of treatments such as adhesion, consolidation or even partial removing of bone to expose unerupted teeth. The different procedures have been identified and are presented in this paper in a chronological succession. Besides, some materials as mortars, which have been historically employed to preserve or to cast this fossil, have been analyzed using X-ray diffraction. Due to the importance of this fossil, a high quality copy has been made based on the patent Nº ES 2 273 577 A1 (Nº 200.501.432), which combines the use of different materials in the same replica thus obtaining more realistic results.

Keywords: fossil preparation; high quality copy; holotype; patent; vertebrates

RESUMO [in Portuguese]

Os últimos processos de preparação realizados no holótipo da espécie *Sinohippus sampelayoi* (Villalta e Crusafont, 1945) (equídeos, Anchitheriinae) foram analisadas. Esta peça singular, uma hemimandíbula localiçada no Museo Geominero desde a década dos 40, foi submetida a um número incomum de tratamentos como a adesão, a consolidação ou a parcial remoção de osso para expor dentes não irrompidos. Os diferentes procedimentos foram identificados e são apresentados neste documento em uma sucessão cronológica. Além disso, alguns materiais como morteiros, que têm sido historicamente utilizadas na preservação deste fóssil, foram analisados por meio de difração de raios-X. Devido à importância do fóssil, uma cópia de alta qualidade tem sido feita com base na patente ES 2 273 577 A1 (Nº 200.501.432), que combina o uso de materiais diferentes na mesma réplica obtendo-se resultados mais realistas.

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INTRODUCTION

"A holotype is the single specimen upon which a new nominal species-group taxon is based in the original publication" (ICZN, 2012; art. 73). Therefore, one of the most important tasks of every museum is the preservation of these bearers of the scientific names of all animal taxa stored in them. According to Brunton et al. (1985), each museum or institution should achieve the following requirements in order to preserve holotypes: 1) ensure that all are clearly marked so that they will be unmistakably recognized as holotype; 2) take all necessary steps for their safe preservation; 3) make them accessible for study and 4) publish lists or catalogues of holotypes in its possession or custody.

The Museo Geominero (Instituto Geológico y Minero de España) holds a significant collection of fossil holotypes which comprise nearly hundred specimens, many of them incorporated in the museum collection during the first half of the 20th century. The holotype of the species *Sinohippus sampelayoi* (Villalta and Crusafont, 1945) (Equidae, Anchitheriinae) from the locality of Nombrevilla (Zaragoza province, Spain) is housed in the Museo Geominero since the 1940's decade (Figure 1). The specimen (MGM-1175M) consists of a right hemimandible with dentition (Villalta and Crusafont, 1945; Salesa et al., 2004), and was part of the permanent exhibition. In order to ensure the adequate preservation of this holotype, it was removed from the exhibition and stored in a secure cabinet together with other holotypes of the paleontological collections. The environment conditions here are very stable, the changes of the temperature, relative humidity (RH), and the quantity and quality of light to which specimens are exposed are minimal. This is the main premise to preserve satisfactorily paleontological materials as this mandible.

A high quality replica has been prepared to replace the specimen preceded by an analysis of its state of preservation. This evaluation has shown that the specimen has undergone a relative high number of different treatments over the years. In order to preserve effectively the sample, it was necessary to know which treatments and materials were used to restore it and how were the procedures employed for each one (Brandi, 1977). The procedures applied on the holotype have been identified, documented and chronologically ordered and are here presented. Besides, a detailed description of the methods followed to prepare the high quality replica is provided.

Figure 1 - MGM-1175M. Right hemimandible of the species *Sinohippus sampelayoi* (Villalta and Crusafont, 1945). A) Lingual view. B) Buccal view. Scale bar 10 cm.

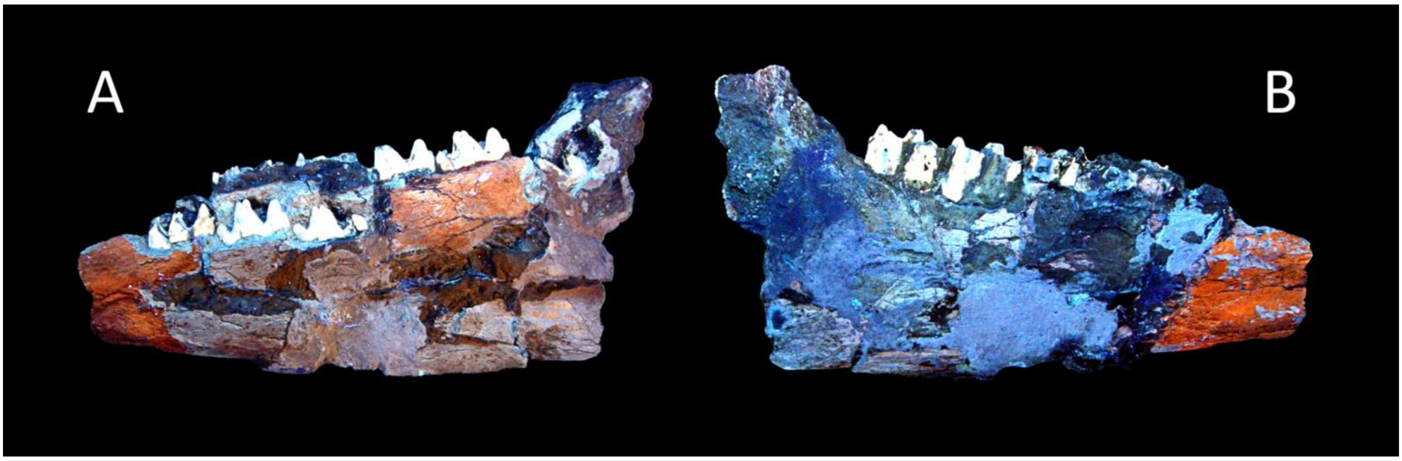

Figure 2 - A) holotype under longwave UV lamp filter and B) holotype under shortwave UV lamp filter.

MATERIALS AND METHODS

Initially the specimen was macroscopically examined and high resolution photographs were taken under different light sources (shortwave and longwave UV lamps; Figure 2). Detailed examination of the specimen was carried out under binocular (Olympus SZX9) in order to assess the presence of different materials and their spatial arrangement.

X-ray powder diffraction (XRD; PANalytical X'pert ProMPD) has been employed to determine the composition of the mortars used in previous procedures. Identifications were made using HighScore version 3.0.4 software (PANalytical) and the ICDD (PDF-2) and COD (January 2012) databases.

After assessment of the specimen preservation and the description of the procedures previously used for its restoration, a high quality replica has been made following the methodology of patent ES 2 273 577 A1 (Nº 200.501.432). All materials used in this process are listed in Table 1.

PREPARATION PROCESS

The specimen (MGM-1175M) has undergone successive preparation procedures which can be sequentially ordered as different materials appear superimposed. Ordering the sequence of materials and events has allowed the differentiation of two main groups of procedures: the ones carried out probably during excavation and those carried out in the laboratory. All of these procedures took place during 40's to 80's decades of the last century, most of which were frequently applied to prepare and preserve fossils at that time (Borselli, 1978).

Treatments during excavation

a) Shellac. Probably used as consolidant. Thin dark layer, covering some areas on both sides of the hemimandible (Figure 3A), which includes small particles and besides is ethanol-soluble, so that an original patina is excluded. Scattered patches can be found on the surface mixed with natural iron oxides spots, which appear interstratified with bone tissue layers.

b) Adhesive 1. Dark colored, cohesive and with bubbles. It has high adhesive capacity (Figure 3B; orange lines).

c) Plaster. Probably used in situ to piece together bone fragments as they appeared poorly preserved (Villalta and Crusafont, 1945; pp. 57; Figure 3C).

Table 1 - Materials used in moldmaking procedures and production of *Sinohippus sampelayoi* replica.

Molding:

DENOMINATION	COMPOSITION	FACTORY OWNER/Store acquisitions
Paraloid B-72	acrilic polymer resin (ethyl methacrylate and methyl acrylate)	*Rhoom & Haas / Manuel Riesgo*:www.manuelriesgo.com/
Silicone RTV-2: *Silastic 3481* (room temperature vulcanizing two components)	Polyxiloxane (SI)	Dow corning / *Feroca:* www.feroca.com/
Catalyzer *Silastic 81 F*	Tetraethyl silicate	Dow corning / *Feroca*: www.feroca.com/
Thixotropic additive *Silastic.*	No facilited	Dow corning / *Feroca* www.feroca.com/
Plasticine, sulphur free	No facilited	*Feroca:* www.feroca.com/ Obtainable in a art store
Carboxymethylcellulose (Demolding)	(Na CMC)	*CTS:* www.ctseurope.com/es/ Obtainable in a Chemical store

Casting:

DENOMINATION	COMPOSITION	FACTORY OWNER/Store acquisitions
FETADIT 55 (Epoxy resin)	No facilited	Fetasa: www.fetasa.es/ Obtainable in a chemical store
FETADIT 56 (catalyst)	No facilited	Fetasa: www.fetasa.es/ Obtainable in a chemical store
Quartz powder	Silical	www.manuelriesgo.com/ Obtainable in a chemical store
Latex rubber	natural rubber	Riesgo: www.manuelriesgo.com/ Obtainable in a art store
Matt and gloss varnish	Inorganic resins	Riesgo: www.manuelriesgo.com/ Obtainable in a art store
Shellac	Organic natural compound	Riesgo: www.manuelriesgo.com/ Obtainable in a art store
Primal SF 016 ER	acrilic polimer (water emulsion)	Rhoom & Haas / Riesgo: www.manuelriesgo.com/ Obtainable in a chemical store
Hebodour, Arquero, Exaduro (Dental Stone plaster)	Calcium sulfate hemihidrate modified	Hërbor España/ Marphil: tienda.marphil.com / obtainable at aceramics supplier or chemical store
Alamo 70 (Plaster of Paris)	Calcium sulfate hemihidrate modified	Hërbor España/ Marphil: tienda.marphil.com / obtainable at aceramics supplier or chemical store
Color pigment powder	Fe Oxihidroxids, sílical	Obtainable in a chemical store

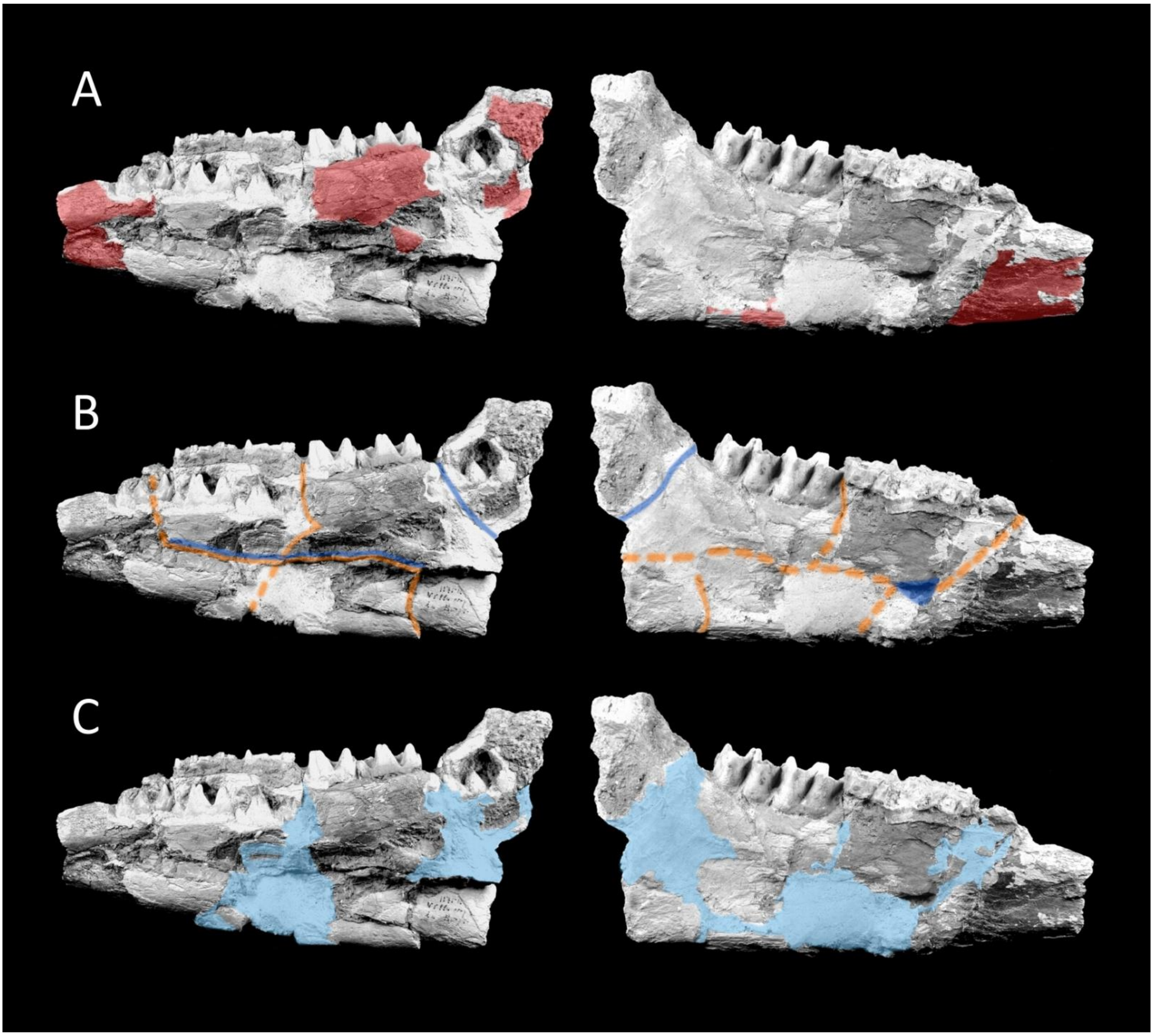

Figure 3 – A) Areas covered with shellac. B) Lines showing rest of adhesives (orange: adhesive-1; blue: adhesive-2). C) Blue areas show the plaster.

Laboratory procedures

a) Coating paint. Greenish layer covering the plaster. It appears mixed with small sized, dark particles (Figure 4A; yellow areas).

b) Coating paint. Yellowish layer covering the greenish coat (Figure 4A; orange areas).

c) Bone removal on the lingual side of the right hemimandible. XR analysis was performed before this procedure (Villalta and Crusafont, 1945; p. 58). Tool marks can be observed (Figure 4B).

d) Adhesive 2. Transparent, with bubbles, poor adhesive capacity (Figure 3B; blue lines), greenish coat (Figure 4A; orange areas).

e) Catalogue number. Handwritten with a waterproof ink pen, probably in the 80's decade. Presently almost faded. Covered with a transparent layer (probably acrylic resin, such as the Paraloid range; Figure 4C).

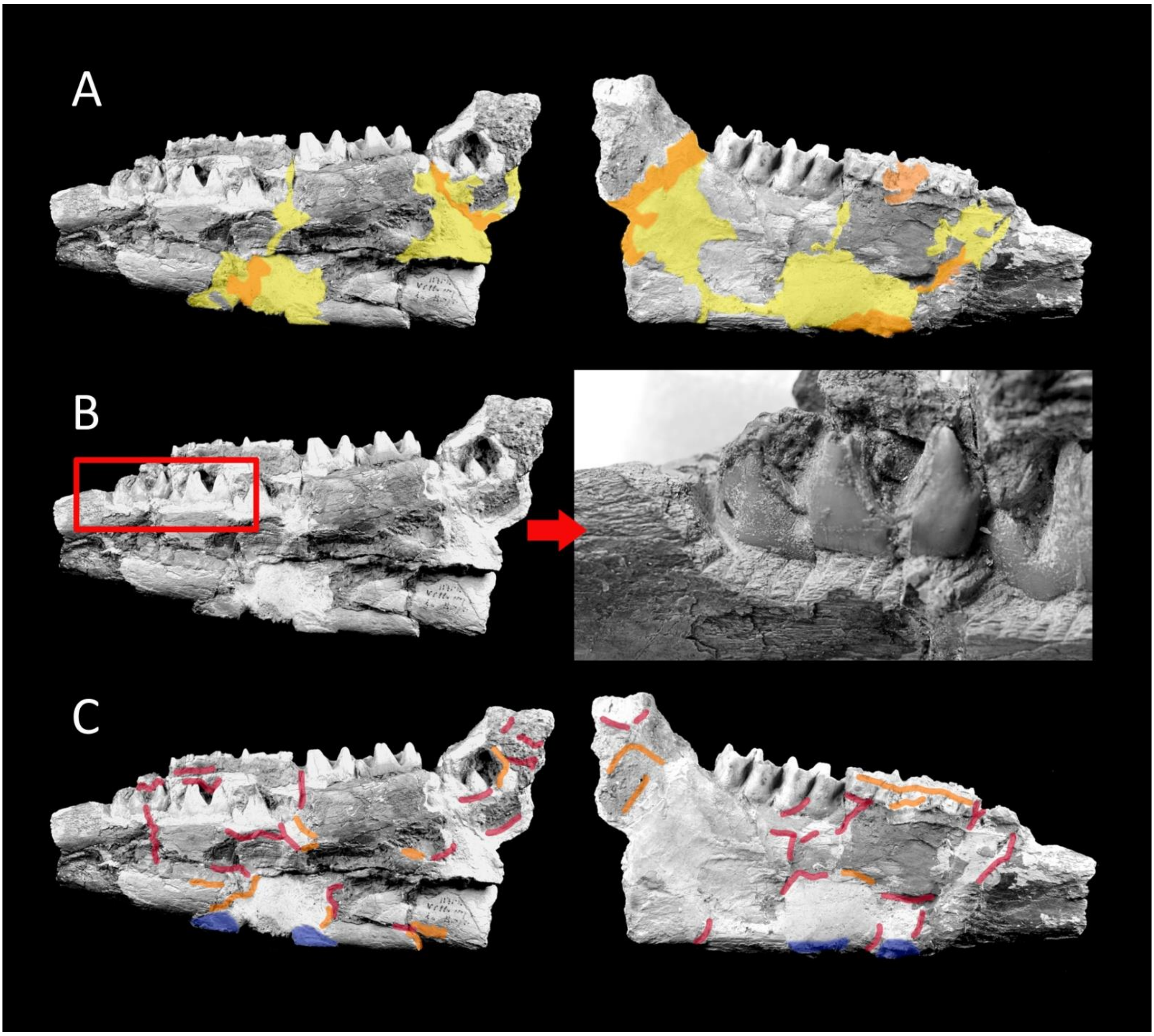

Figure 4 – A) Coating paints on the plaster. B) Bone removed area (inset) and detail of tool marks. C) Colored lines showing the distribution of extraneous materials (red: silicone rubber; orange: plasticene/wax; blue: blu-tack).

f) Coating varnish. It covers the entire specimen surface, probably as a protection before previous casting and molding processes. Rests of white silicone are found in many original cracks of the specimen. This silicone had low viscosity and was mixed with a slow catalyst (Figure 4C; red areas). Besides, a bluish material (Plasticene ™ or wax) is widely distributed over sides of the specimen (Figure 4C; orange areas).

g) Blu-tack. Reusable adhesive putty used for holding the specimen in the exhibition (Figure 4C; blue areas).

XRD-Analysis

Some mortars have been analyzed using X-ray diffraction to determine its composition. They are the most vulnerable (due to their own features) to changes in relative humidity of all different materials employed to preserve the fossil. Gypsum is the main mineral identified by XRD although traces of Bassanyte are also present (Figure 5). Bassanyte is a hemihydrate ($CaSO_4 \sim 0.5H_2O$), while the dihydrate ($CaSO_4 \cdot 2H_2O$) occurs naturally as gypsum. However Bassanyte, better known as plaster of Paris, occurs exceptionally in nature. It is equivalent to plaster used in many preparation procedures. In the case of the analyzed holotype, the presence of Bassanyte is unexpected because plaster of Paris (Bassanyte) was mixed with water to made plaster. During hardening of this plaster, the Bassanyte must recover the two initial molecules of water (Gypsum). The presence of Bassanyte could be related to an occasional heating of the sample, but this hypothesis can be rejected due to the good preservation condition of the sample. Although a considerable amount of literature has been devoted to the crystallography of hemihydrate, there are still a number of unresolved problems (Lager et al., 1984). The plaster used on the holotype was probably added with an animal glue solution because of the high tenacity observed in these parts of the sample. Mixing plaster of Paris with an animal glue solution, as a most used material for mortars, was a very frequent procedure during 19th century. Further analyses should be necessary for accurate identification of the materials utilized in these historical procedures. Adhesives, wax and lacquers could be analyzed using gas chromatography mass and x-ray diffraction (crystalline compound).

REPLICATION PROCESS

After the identification of the different materials which cover the specimen and the assessment of its preservation condition, a replica has been created following four phases:

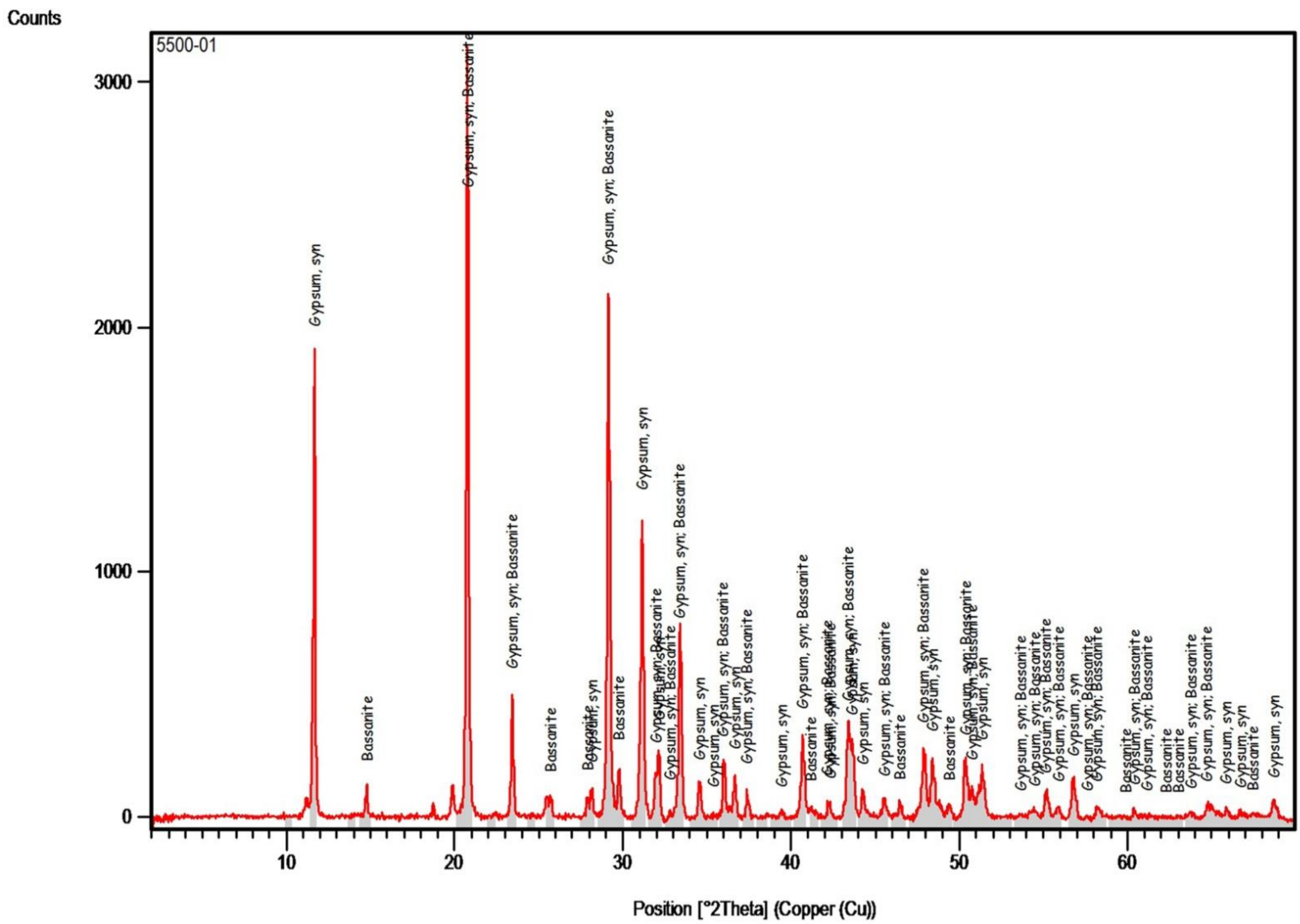

Figure 5 - X-ray powder diffraction (XRD) diagram of material analyzed.

Phase A: Pre-treatment

a) The specimen was completely coated with a thin protecting layer of consolidant. Small superficial holes and fissures were filled using Paraloid B-72 (15% in acetone). This step is of main importance for avoiding damage of the specimen and improving the quality of the final cast.

b) Given the nature of materials and waterproofing of the original piece it was decided to apply Carboxymethylcellulose (2% in water) as a layer to make easier to remove the mold. Then, two-part thin-walled poured mold and two jackets were made following the morphology and size of the specimen.

Phase B: Molding

a) A two part poured mold with openings for entrance of fluid silicone rubber was made. Then, a Plasticine™ layer was prepared for coating the holotype which was previously protected with Polyethylene film. Besides, a security Plasticine™ cord to avoid losses of silicone rubber and connect the first side of the mold was applied.

It is important to point out that, the Plasticine™ seam line should be placed in a way that covers the least amount of information on hidden parts of the specimen as this line should be. However, in this case the seam line was placed around the teeth.

b) Both silicone rubber molds were overlaid by a middle hardness stone plaster (Alamo 70).

The first part of the jacket was made, after the first part of the mold has set, in the same manner as for a one part mold.

Phase C: Casting

This phase follows the method described in Licence "Proceso de reproducción de fósiles, rocas y minerales y producto obtenido", ES 2273 577 A1 (Nº 200.501.432).

a) In a first phase, a master of the dentition in a first casting was obtained. In this case, it was used a dental quality plaster material which was poured on a silicone rubber mold in order to achieve a sub mold what was used to obtain a final casting in Epoxy resin. Finally a polychrome layer was applied.

b) Next, the dentition and the bone structure of the specimen were molded independently.

b.1 Dentition: Casting in Epoxy resin.

A mixture of a resin basis (*Fetadit 55)* and a catalyst *(Fetadit 63)* plus quartz powder (ratio 2:1:2) was used in order to achieve a similar appearance to the original piece. Then, small attachments were inserted in the resin when it was still in a mordant state. Thus both parts (resin and dental plaster) were connected to each other and afterward the resin dentition was coated by a thin layer of latex rubber like a layer protector.

b.2 Bone structure: Casting in dental plaster (Arquero; Figure 6C).

First, the fluid dental plaster was subjected to air extraction in order to remove air bubbles. The previously prepared wall silicone rubber mold was completely coated with a thin layer of this plaster and then a second thicker layer was applied.

Finally, once the copy of the specimen was separated from the silicone rubber mold, it was cleaned and the latex rubber removed

Phase D: Casts coloring

a) Both parts of the replica were colored following next steps:

a.1 Dentition: Color working of Epoxy resin.

The chromatic range of pigments used consisted of: brown, white, black, reddish pigments. A varnish mixture was used as medium: matt varnish and gloss varnish plus shellac, the latter offering optimum results.

Brown pigment diluted in ethanol was applied using a soft bristle brush (Figure 6A). Then a piece of cotton was used to remove the excess of paint and to highlight the textures across dentition.

Varnish layers plus white and yellow pigments were also applied (Figure 6B).

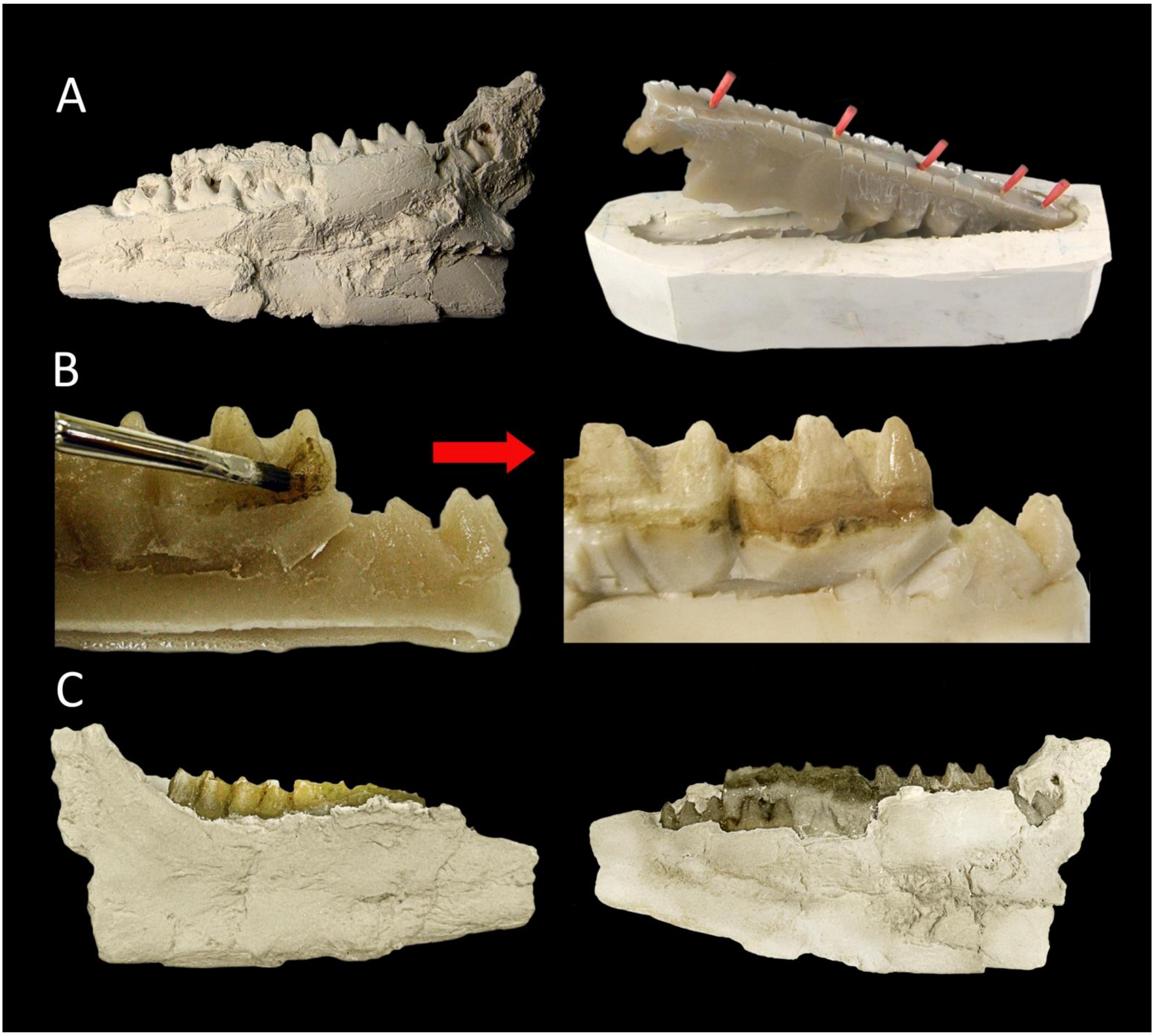

Figure 6 **–** A) Master on dental plaster and sub mold corresponding to the teeth. B) Detail of teeth and polychromed process. C) Appearance of the replica that is composed of two different materials.

Finally, a dry mixture (Talc plus brown and white pigments) was applied after the varnish layers dried.

a.2 Bone structure: Color working of dental plaster.

A thin color layer was applied over the plaster using Primal (5% in water) plus grey pigment in order to get a waterproof surface. Next more color layers were applied (Figure 7A).

To color other zones, we used a mixture based on Primal plus grey pigments (Figure 7A).

In order to obtain a color similar to the original specimen, fine details were applied using a mixture of shellac and brown pigments (Figure 7B).

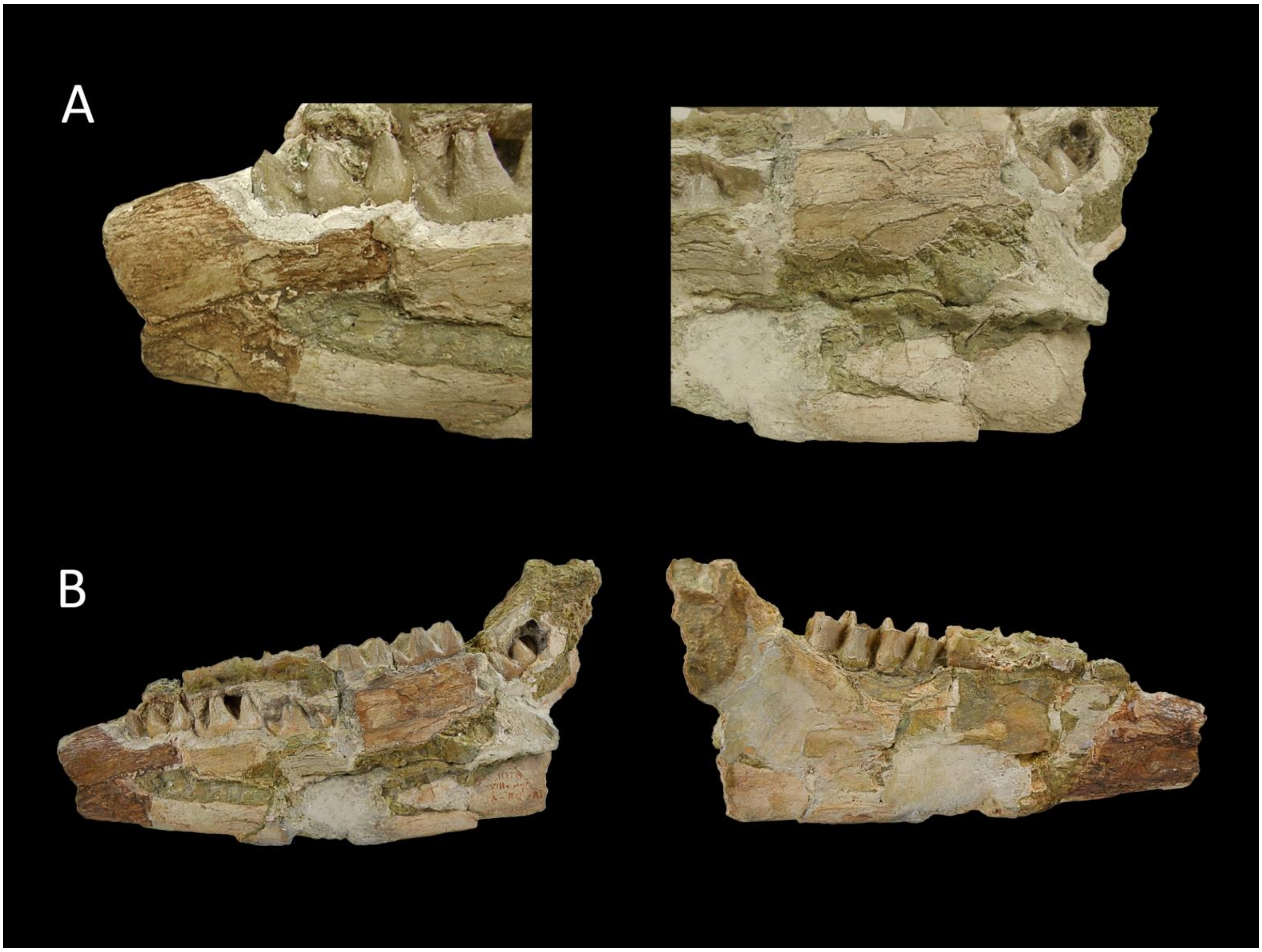

Figure 7 - A) detail of process of patination, B) finished replica in lingual and buccal view.

CONCLUSIONS

The detailed analysis of the holotype MGM-1175M before molding has allowed the identification of previous preparation procedures, which have been presented chronologically ordered. All the methods employed have modified the specimen structure (bone removal, fragments assembling with plaster and adhesives), the coloration (shellac, paints) and have added extraneous material (silicone, wax, Plasticine™).

The record of the observed modifications on the sample and the identification of the materials are of main importance for: 1) assessing the state of preservation of the specimen before molding and 2) for monitoring the stability of the material employed. This is an essential point considering that plaster (with contaminants but not detected by XRD) is hygroscopic, thus the stability of relative humidity conditions is indispensable. To avoid this possible damage, an impermeable layer (acrylic pigments and shellac) is protecting the holotype, and a Paraloid B-72 layer was employed to protect the part where the analyzed sample was extracted.

A high quality replica of the holotype MGM-1175M has been made using the patent Nº ES 2 273 577 A1 (Nº 200.501.432), which combines the use of different materials in the same copy. This replica will be useful for different purposes (exhibition, education, loans) and simultaneously will permit the preservation of the holotype under appropriate environmental conditions.

To preserve original specimens is a main task for specialists and of main interest for the society. The demand for protection of this kind of unique and valuable pieces is increasing (Baeza et al., 2013). In this context, the implementation of the Patent is of main interest. In the same manner, diversity of products and their modifications in global market in order to produce replicas and facsimiles is huge, as are new surfaces finish quality and polychrome works possibilities too. Products used in paleontological restoration have evolved from low quality, instability, highly fragile plasters, going through polyester resins reinforced with glass-fiber to modern materials: acrylic resins, high density polyurethane with sensitive UV filters, among others. All of them have been categorized as long-lasting materials with stable charging elements which have been added becoming indistinguishable pieces from original specimens at first visual exam as in the case of facsimiles (Pereira Prado, 1999 a, b). Above all, replicas represent an excellent way to guarantee the preservation of an unique natural heritage as fossil holotypes are (Baeza and Lozano, 2009).

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REFERENCES CITED

Baeza, E., and R. P. Lozano. 2009. Environment Conservation Problems in the Geological Collections of The Museo Geominero (IGME, Geological Survey of Spain, Madrid). Paleontologia I Evolució Memòria especial 4:11–26.

Baeza, E., A. Rodrigo, and R. P. Lozano. 2013. La importancia de las réplicas en la investigación, conservación y difusión del patrimonio Geológico mueble. XX Bienal de La Real Sociedad de Historia Natural. Libro de Resúmenes 6–7.

Borselli, V. 1978. Técnicas modernas de recuperación y reproducción de material fósil. Coloquios de Paleontología 33:29–34.

Brandi, C. 1977. Teoría de La Restauración. Giulio Einaudi Editore, Torino, Italy, 152 pp.

Brunton, C. H. C., P. T. Besterman, and J. A. Cooper. 1985. Guidelines for the Curation of Geological Materials. Geological Society, London, UK, 218 pp.

ICZN. 2012. The International Commission on Zoological Nomenclature, 4th Edition. International Trust for Zoological Nomenclature, London, UK.

Lager, G. A., T. Armbruster, F. J. Rotella, J. D. Jorgensen, and D. G. Hinks. 1984. A crystallographic study of the low-temperature dehydration products of gypsum, CaSO4.2H2O; hemihydrate, CaSO4.5H2O, and gamma-CaSO4. American Mineralogist 69:910–919.

Pereira Prado, C. 1999a. Facsímiles de objetos de arte tridimensional 1ª parte: Moldeo. Restauración & Rehabilitación 66–71.

Pereira Prado, C. 1999b. Facsímiles de objetos de arte tridimensional 2ª parte: vaciado. Restauración & Rehabilitación 66–71.

Salesa, M. J., I. M. Sanchez, and J. Morales. 2004. Presence of the Asian horse *Sinohippus* in the Miocene of Europe. Acta Palaeontologica Polonica 49:189–196.

Villalta, J. F., and M. Crusafont. 1945. Un *Anchitherium* en el Pontiense Español *Anchitherium sampelayoi*, nova sp. Notas Y Comunicaciones Del Instituto Geológico Y Minero de España 14:51–82.

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UNFAVORABLE MICROCLIMATE CONDITIONS IN EXHIBITION ROOMS: EARLY DETECTION, RISK IDENTIFICATION, AND PREVENTIVE CONSERVATION MEASURES

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ABSTRACT

This paper discusses the variability in space and time of microclimate in exhibition rooms and the related impact on collections composed of organic materials. The main deterioration mechanisms and risk assessment tools are highlighted. The historic climate, recommended by the EU standard EN 15757:2010 to avoid mechanical damage for the conservation of organic hygroscopic materials is elucidated. The limits of tolerable temperature (T) and relative humidity (RH) variability on the long (seasonal) and short time-scale (fluctuations) are also presented. The uneven distribution of heat in a room, especially in the corners or behind furniture, creates a habitat favorable to mold infestation. Special temperature T and RH diagrams, produced under the EU funded "Climate for Culture" project, are useful to assess risk for infestation by insects and molds, as well as the risk of damage (deformation, cracking, or blistering) for wooden objects or polychromy. A discussion concerns the possibility of killing insects and molds with high or low temperatures, or using the vacuum cleaner. The lifetime of cellulose (paper and textiles) is also considered. The exhibition lighting is considered in light of two EU standards, i.e. CIE 157:2004 and CEN TS 16163: 2014. The standards provide useful recommendations about light sources, emission spectra, illuminance, and upper limit of annual luminous exposure for photosensitive surfaces. Finally, the paper presents the EU standard EN 15999-1: 2014 that is a guideline for design of showcases for exhibition and preservation of collections. It provides general instructions to reduce the risk of physical damage to exhibits (e.g. theft, vandalism, natural disasters) and to improve the control of environmental parameters (e.g. T, RH, dust, pollutants and light).

Keywords: European standards; museum conservation; organic materials; microclimate; pests

RESUMO [in Portuguese]

Este artigo discute a variabilidade no tempo e no espaço do microclima em salas de exposição e o impacto nas coleções compostas por materiais orgânicos. Os principais mecanismos de deterioração e ferramentas de avaliação de riscos são apontados. O clima histórico, recomendado pelo standard EN 15757:2010 da UE para evitar danos mecânicos à conservação de materiais orgânicos higroscópicos é elucidado. Os limites toleráveis de variação de temperatura (T) e humidade relativa (RH) em longa (sazonal) e curta escala de tempo (flutuações) são também apresentados. A distribuição desigual de calor numa sala, especialmente nos cantos e por detrás de móveis, cria um habitat favorável a infestações de bolor. Diagramas especiais de T e RH, produzidos ao abrigo do projecto "Climate for Culture", financiado pela UE, são úteis na avaliação de risco de infestação por insectos ou bolor, bem como do risco de danos (deformação, formação de bolhas e fendas) para objectos de madeira ou policromia. Discute-se a possibilidade de matar insectos e fungos com altas ou baixas temperaturas, ou usando um aspirador. O tempo de vida da celulose (papel e têxteis) é também considerado. A iluminação em exposições é considerada à luz de dois standards da UE, i.e. CIE 157:2004 e CEN TS 16163:2014. Os standards dão recomendações úteis sobre fontes de luz, espectro de emissões, iluminância e limite superior de exposição luminosa anual para superfícies fotossensíveis. Finalmente, este artigo apresenta o standard da UE EN 15999- 1:2014 que é o guia para o design de armários para exposições e preservação de coleções. Providencia instruções gerais para a redução de risco de danos físicos a exposições (por exemplo, roubo, vandalismo, desastres naturais) e para a melhoria do controlo de parâmetros ambientais (por exemplo, T, RH, pó, poluentes e luz).

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INTRODUCTION

It is well known that the conservation of collections composed of organic materials is strongly determined by the indoor climate. In general, the main deterioration mechanisms are known. Conservators take care to keep ideal conditions recommended in standards or internal regulations or, at least, to avoid situations involving high risk, e.g. extreme temperature (T) and relative humidity (RH) levels, or abrupt T and RH changes, or enhanced T and RH fluctuations in amplitude and duration.

This paper has the following aims: to give an answer to some crucial questions, to limit misinterpretations and misuse of standards and recommendations, to provide a helpful survey of the main topics, and to assist the user in preventive conservation by making clear the relationship between climate and risk of degradation for some key materials in museum collections.

The first question concerns the indoor climate: Where, in the room, T and RH should be monitored? T and RH vary from one point in the room to another. If you are concerned about shrinkage/swelling, condensation/evaporation, corrosion, pest infestation, or any other decay mechanism, you should not be vaguely interested in what is happening in the air, but rather on the surface of objects in your collections and how they interact with the air. Phenomena occurring at object surfaces account for the variety of decay we can observe in the same room and even on the same object.

Any object composed of organic materials undergoes deterioration mechanisms determined by its temperature and the moisture either adsorbed on the surface or absorbed inside the material. The moisture content of a hygroscopic material is ultimately related to the T and especially the RH in the air, so when the material is exposed to a given T and RH value, the constant equilibrium moisture content is eventually attained. Therefore, when the indoor climate is variable, the air and the materials are not in equilibrium, and the measurements taken in air are only partly representative of the objects inside a room. Departures from the equilibrium may become larger in the presence of lighting, or when heating, ventilation, or air conditioning (HVAC) systems are used. A crucial point is how to practically control the microclimate and to timely assess risk of damage.

In order to increase the preparedness for responding to global warming and preserving the European cultural heritage, the EU funded "Climate for Culture" (CfC) project was focused on the simulation of the indoor environmental changes that would likely occur in the 2021-2050 near future and 2071-2100 far future, and to assess the related risk factors for cultural heritage materials. In the following some CfC risk evaluation tools and simulated scenarios will be shown as elucidative examples.

HOW HOMOGENEOUS IS CLIMATE IN A ROOM?

Inside a room the temperature is not homogeneous for a number of reasons (e.g. heat sources and exchanges, air movements and leakage, thermal conductivity of the envelope), and a record of T and RH taken in the middle of the room, or in a corner, is rarely representative of the climate experienced by the collection; for example paintings hung on walls. An example of how variable T and RH may be within an exposition room of a museum is shown in Figure 1. In this room, the distribution of T and RH are affected by visitors, the HVAC system, and the air motions from one room to another. If the sensors to monitor or to control the indoor climate are located in positions where T and RH are different from the real situation of exhibits, the monitoring may be not adequately representative, or even misleading.

However, the situation may not be homogeneous, not only in a room, but also within a single wall. The paintings hung on the walls of the gallery selected for the example in Figure 2, when observed in the thermal infrared (IR) wavelength with a thermocamera, show a wide range of variation, especially at the blinded windows behind panels and painting frames. Paintings are hung on panels constituting a second thin wall parallel to the main one, to avoid internal light reflections and increase the exposition area.

The non-homogeneity of the surface temperature reflects a non-homogeneity of the RH at the interface between the paintings and the air. This can be calculated using the observations of surface temperatures and the humidity mixing ratio in the air as recommended in Section 5 of the EU standard EN 16242: 2012: "Considerations and recommendations related to measuring"

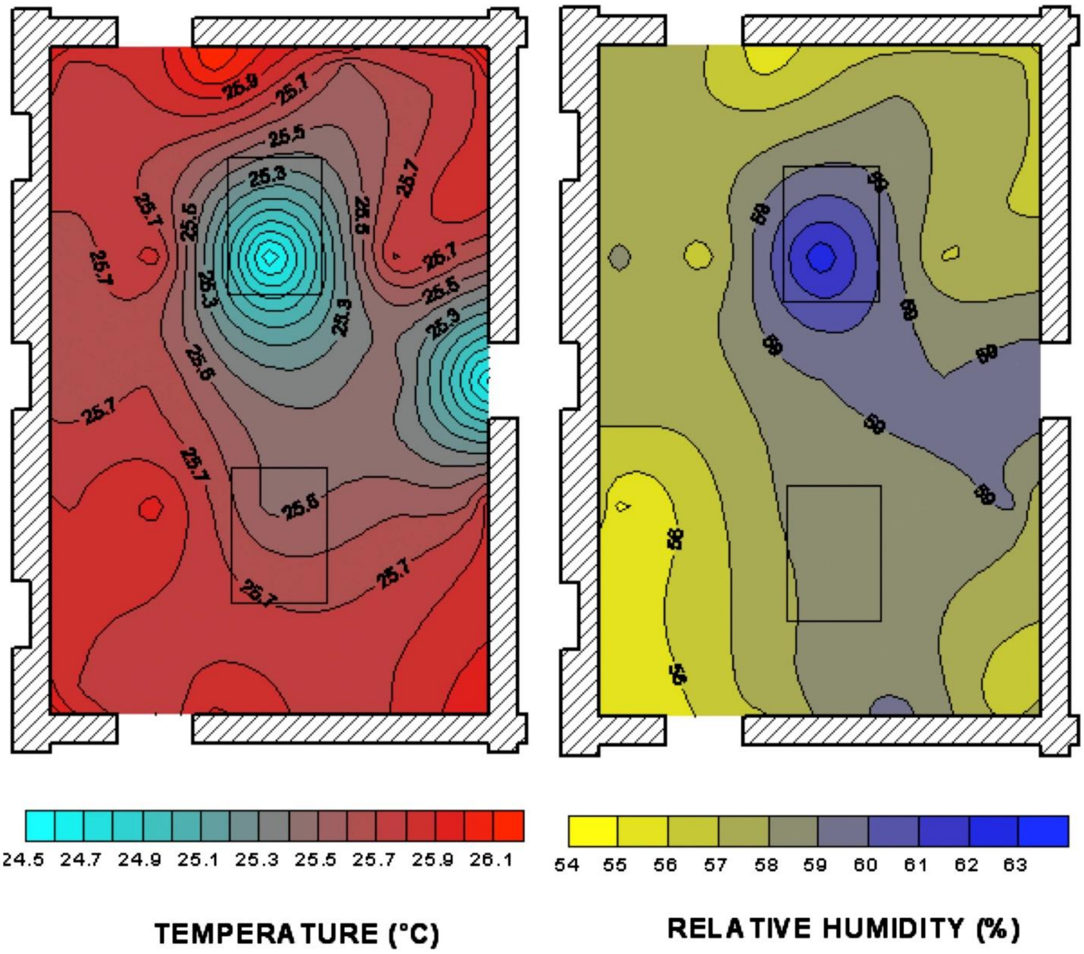

Figure 1 - Temperature and relative humidity in an exhibition room of an art museum.

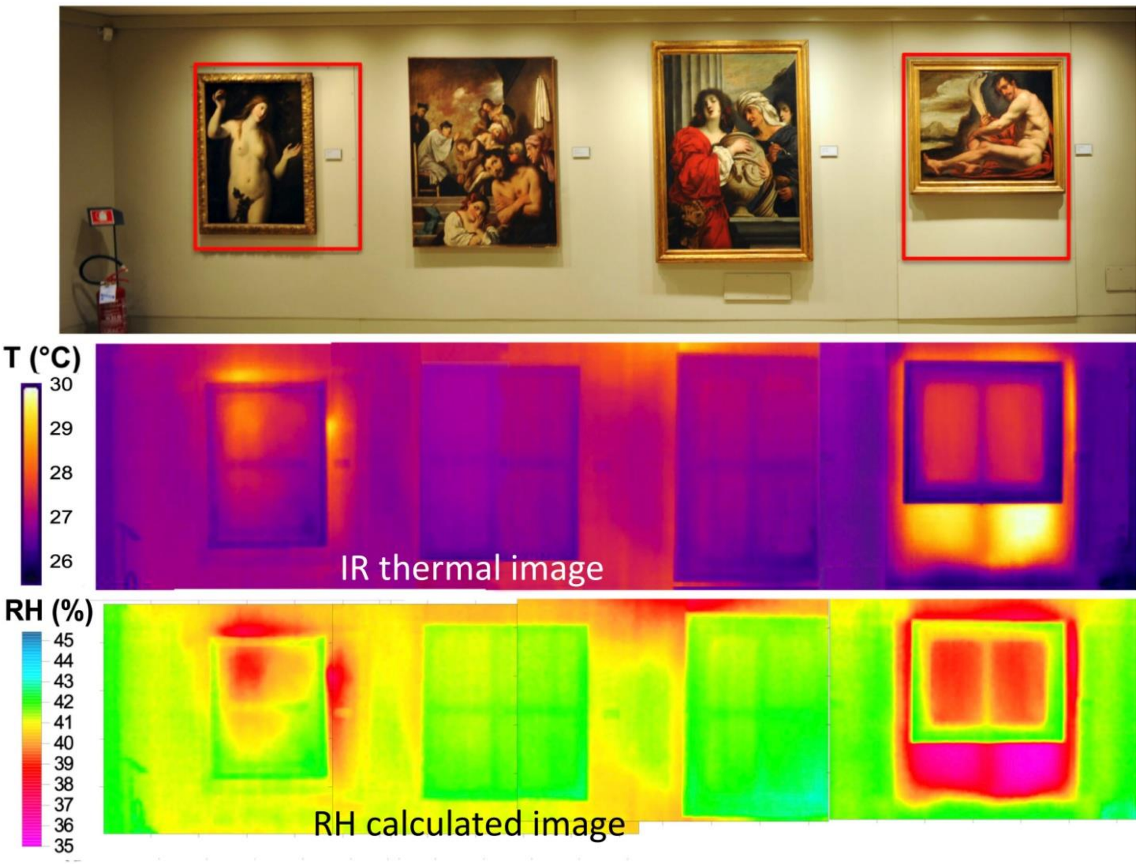

Figure 2 - View in visible light of paintings hung on a wall of a gallery; thermal image of the same wall taken with a thermocamera in the near infrared; image of the relative humidity at the interface between the air, the paintings and the wall, calculated using the temperature of the surfaces and the moisture content in the air.

on the procedures and instruments for measuring humidity in the air and moisture exchanges between air and cultural property. This is the simulation of the RH calculated in the viscous air layer in contact with the surface. The temperature is determined by the materials, and the moisture content is the same as in the free air at some distance from walls, because of the high diffusivity of the water molecules (Camuffo, 2013). In the picture, the RH simulation allows us to see when, where, and how much RH departs from the average levels in order to undertake measures for preventive conservation.

Inside a room, some natural ventilation is generated by local thermal unbalances, leakage, etc. Natural ventilation is slow and often not perceived at all, but in any case it is a powerful motor that redistributes heat within the room. Air movements may be generated by heaters operating in the cold season, down draughts along cold windows or walls, external warm air entering the room, lighting systems, or any temperature imbalances inside a room or between adjacent rooms. Walls are well ventilated, receive heat, and reach mild temperatures. Corners, however, are less ventilated, receive less heat, and their temperature is lower (Figure 3). As a consequence, corners have higher RH and, consequently, the local moisture content of walls in equilibrium with the ambient air is also higher. If the moisture reaches the threshold for mold colonization, fungi sporae may germinate and will colonize the corner.

The same occurs behind furniture close to a wall (Figure 4). In the cold season, the heat generated inside flows outside in various ways, e.g. by air leakage or heat loss across the envelope. Let us concentrate on the heat loss across a wall. The heat flow is inversely proportional to the resistance offered by the wall, and the internal surface of the wall assumes the temperature level of the air, decreased by an amount determined by the heat loss across the wall. When furniture is located close to a wall, the thin air layer between the back of the furniture and the wall

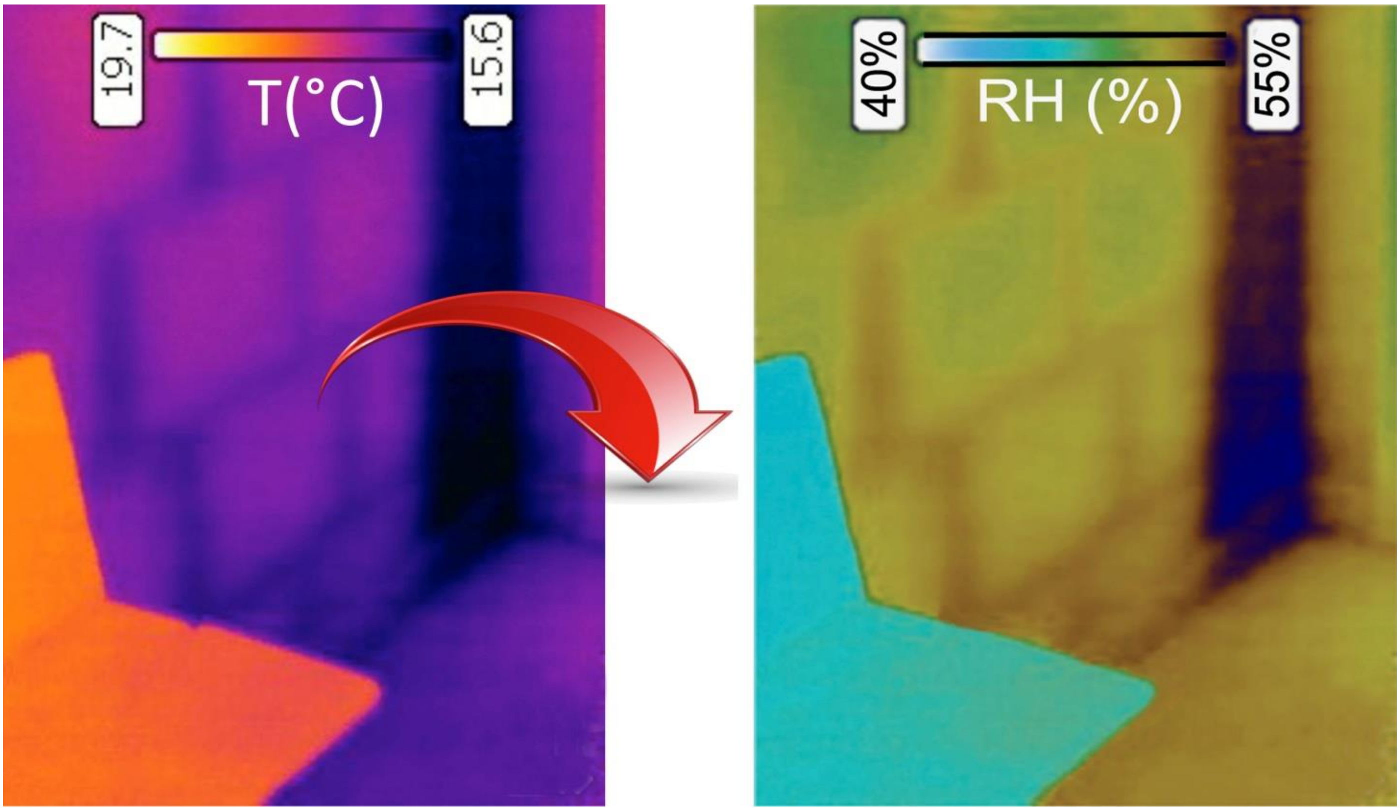

Figure 3 - Thermal image of a cold corner in a heated room in winter, taken with a thermocamera in the near infrared; image of the relative humidity at the interface between the air and the wall, calculated using the temperature of the surfaces and the moisture content in air. The arrow shows the internal air circulation. A warmer bench (at indoor air temperature) is visible on the left side.

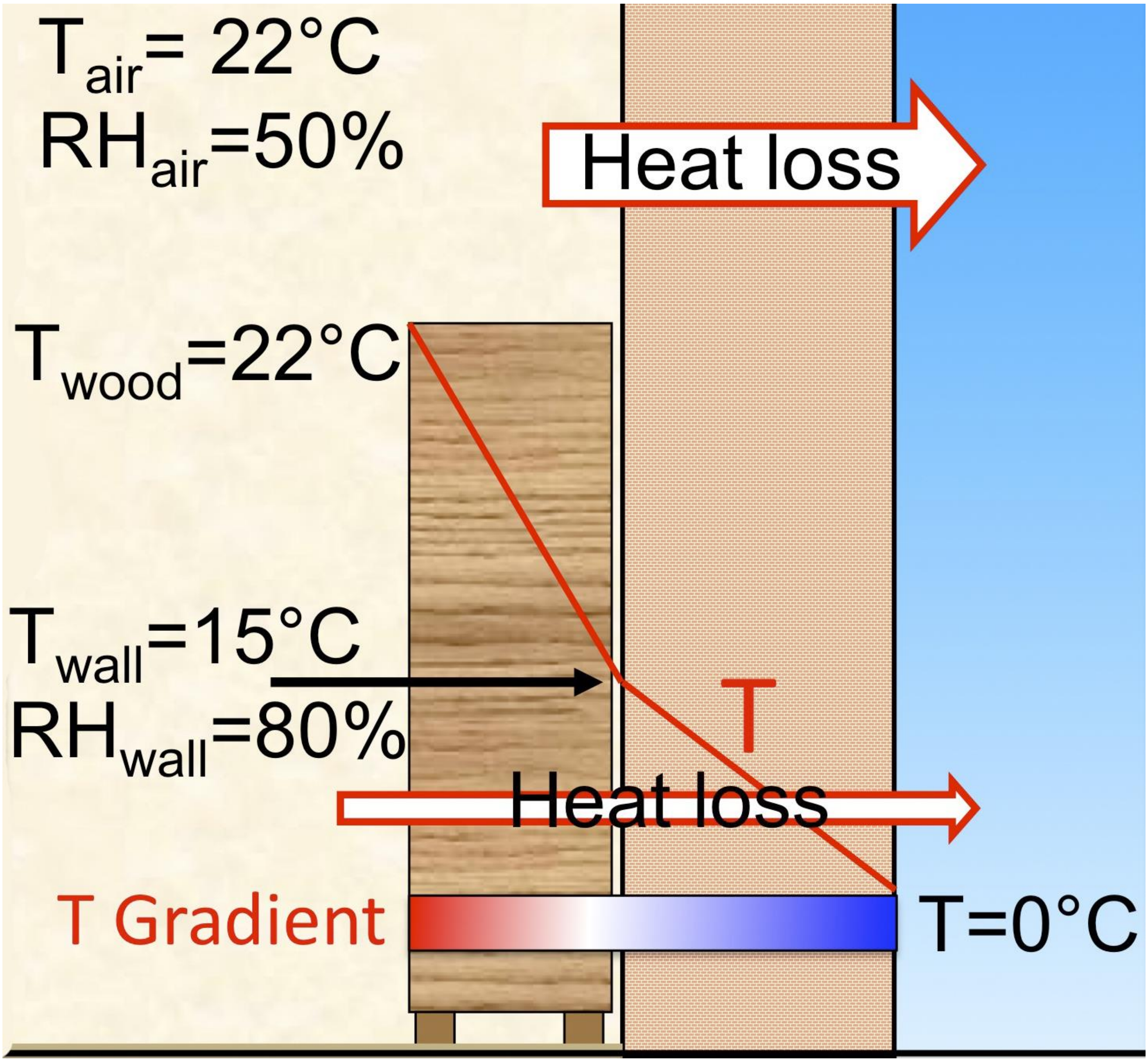

Figure 4 - An example to explain why molds grow behind furniture. Walls release heat to the exterior. In the absence of furniture, the wall surface receives heat and is relatively warm (e.g. T=20°C). When furniture is located close to it, the heat supplied (from ventilation) to the wall is reduced and its temperature falls (e.g. T=15°C), raising RH (e.g. 80%) and the equilibrium moisture content of plaster. This situation constitutes a favorable habitat to mold development.

reaches a new equilibrium. The moisture content in the air remains the same for the high diffusivity of the water molecules, but the heat transported by ventilation is strongly reduced. The furniture acts as a thermal insulator in front of the wall. This portion of wall receives little heat across the furniture and the thin air layer, and consequently its temperature drops. The RH in the thin air layer increases accordingly, possibly reaching the threshold for mold colonization. The problem may be simply solved by increasing the distance of the furniture from the wall, allowing better ventilation and heat transport.

The above examples show that a room with excellent indoor climate may locally reach unsafe conditions, depending on the use of the room, the HVAC systems, the location of furniture, and many other factors that may affect the local exchanges of heat and moisture and the resulting microclimate.

It is evident that records of T and RH taken in the free air inside a room are useful, but only vaguely representative of what is happening on the surfaces: some objects may be in equilibrium with the air, others, at higher temperatures, may be releasing heat and moisture, and still others, at lower temperatures, may have the opposite flows or even condensation. For this reason, climate monitoring in a museum should not only provide a general idea of the T and RH levels of the air in each room, as is usually done, but it should also determine what specifically happens at the interface with each exhibit of the collection, by monitoring its temperature with a thermocamera and calculating the corresponding RH level at the interface with the air, as discussed above.

Corners and other particular positions should be carefully investigated even in cases when they do not host collections. The reason is that, if they constitute a convenient habitat for molds, they will be colonized and risk to disseminate sporae and infest the whole room, or even the whole museum.

HISTORIC CLIMATE, ARTIFICIAL CLIMATES, AND THE CONSERVATION OF ORGANIC HYGROSCOPIC MATERIALS

It is obvious that the ideal condition would be to keep collections in an absolutely stable environment, with T and RH constant over time and fixed with negligible fluctuations at levels convenient for the materials and unfavorable to pests. The variability of T and RH has been considered in the guidelines for museum indoor conditions developed by ASHRAE (2003, 2007). Museums and galleries are categorized in six climate classes, i.e. AA, A, A, B, C, D, from smaller to larger variability of T and RH either seasonal or short-term. The top classes are not sustainable due to the high cost-benefit ratio and not justified in a museum management. The problem is to know which T and RH variations vulnerable objects can tolerate.

ASHRAE (2003) introduced the concept of "proofed fluctuation", i.e. the largest RH or T fluctuation to which the object has been exposed in the past without having suffered visible damage. It was supposed that the risk of further damage from fluctuations smaller than the proofed value is extremely low (Michalski, 2009). However, it has been observed that extreme T and RH fluctuations may generate internal micro-cracks, and these may subsequently grow with repeated stress/strain cycles until they form macro fractures as expansion joints to respond to the climate variability (Bratasz et al., 2007; Bratasz 2010). Laboratory tests and field observations have concluded that hygroscopic organic materials are highly vulnerable to RH changes, and less to T. In addition, the safe variability interval depends on the initial RH conditions to which the object was acclimatized.

The EU standard EN 15757:2010 concerning the specifications for temperature and relative humidity to limit climate-induced mechanical damage in organic hygroscopic materials defines the "historic climate" (HC) as the climate conditions in a microenvironment where a cultural heritage object has always been kept, or has been kept for a long period of time (at least one year), and to which it has become acclimatized. This concept is fundamental for the conservation of wood, books, and other objects, especially when they are composed of different materials or when different parts of the same material are joined together (Camuffo, 2010, 2013). The historic climate considers that an object composed of materials characterized by different degrees of expansions or contractions may be severely damaged by climate changes (especially RH changes). Any change in RH implies a change in the moisture content and a deformation in shape or size (strain). The damage derives from the internal forces (stress) generated by the departure from the basic RH level in which the object was kept and to which it has been acclimatized (Mecklenburg et al., 1998; Bratasz et al., 2007; Bratasz 2010). The acclimatization may have caused structural transformations, e.g. plastic deformations and/or fractures. However, once the object has been acclimatized, it reaches a new structural equilibrium with the final RH level.

From a practical point of view, the conservator should periodically control the collections. If an object is found to be in bad conditions, it is necessary to search for a remedy, studying the object and its environment, i.e. causes and effects. On the other hand, when objects are in good conditions, it is dangerous to change the climate and enter an unknown, unsafe area. The historic climate should be kept unchanged to avoid mechanical stress and damage. However, it may happen that an object is moved from its original place to another location (e.g. temporary exhibition, new building) or a HVAC system is planned or installed in the room, or its use may imply T and RH unbalances. In other terms, any historic climate is characterized by a certain long-term variability (e.g. seasonal cycle) and a number of short-term fluctuations (e.g. due to window opening, HVAC operations). The combination of the long-term and short-term RH variability defines a band whose upper and lower limits are determined by extreme RH levels, i.e. peaks and drops in RH. Extreme RH values may be risky because they may have triggered dangerous strain-stress cycles with micro-fractures inside the material. The repetition of extreme cycles (i.e. the accumulation of strain-stress cycles) may lead to macroscopic mechanical damage. For this reason the standard recommends staying at a prudent distance from the RH extremes on either side (too dry - too humid), excluding the 7% of the highest and the 7% of the lowest readings. This means that the safe band lies within the 7^{th} and 93^{rd} percentiles of the fluctuation magnitudes (i.e. a fluctuation is calculated as the difference between a current RH reading and moving average calculated for the whole calendar year with a 30-day window).

For instance, the EU standard EN 15759-1: 2011 focused on guidelines for heating churches, chapels, and other places of worship states that churchgoer thermal comfort and cultural heritage conservation may be conflicting. If a compromise is not acceptable, cultural heritage and the historic climate defined in EN 15757:2010 shall have priority. Practically, in the case an object should be moved from one ambient to another, or a climate control is installed, it is necessary to pass through three steps: (i) Knowledge of the historic climate (HC). If the HC is not known, it is necessary to measure it for one year; (ii) Staying within the 7^{th}-93^{rd} percentile safe band (to remain in the HC); (iii) Verification that the new room, or the HVAC, complies with the HC, at least in close proximity to the object.

A useful tool to assess the risk of yield or failure of wooden sculptures, and of cracking and delamination of decorative layers has been obtained by plotting matched pairs of observed and averaged RH levels in a diagram obtained from laboratory tests (Martens and Schellen, 2013). The observed instantaneous RH levels are representative of the continually changing moisture content in the surface layer, while the averaged RH levels are representative of the equilibrium in the internal layers. The depth of the internal layer is related to the time required for heat and moisture to diffuse inside the material, i.e. the response time of the object. The difference between the instantaneous and averaged RH data is representative of the strain and stress inside the material. In the risk assessment diagram, matched instantaneous and averaged RH readings are plotted, and they may fall in the safe (green) area, or in the areas where objects are endangered by permanent deformation (yellow) or failure (red), as shown in Figure 5 for wooden sculptures (left diagram) and panels (right diagram).

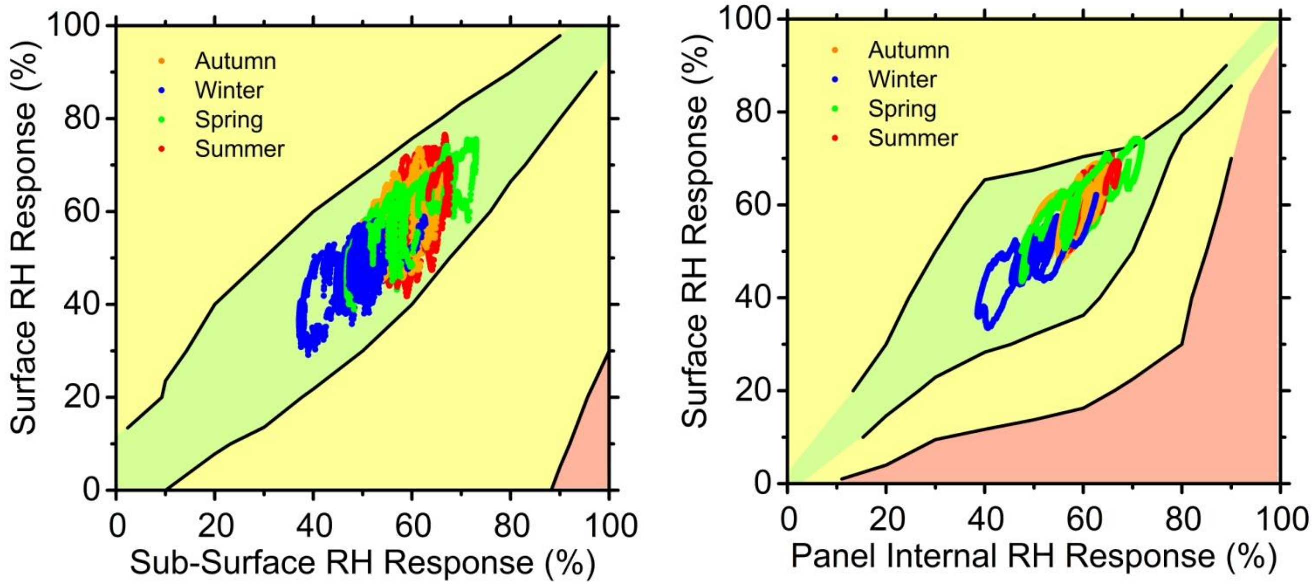

Figure 5 - Example of microclimate risk assessment tool for a wooden sculpture (left side) and a panel painting (right side) kept in an unconditioned building type 02 of the Climate for Culture Project. Green area refers to safe conditions with reversible changes; yellow to conditions endangering objects by deformation; red by possible failure. Color dots refer to RH readings in spring (green), summer (red), autumn (orange) and winter (blue). Note: The building type 02 represents a small, heavy weight building (Floor Area ≈ 245 m^2, Volume ≈ 2600 m^3, sandstone wall with 1.25 m thickness and 2 cm thickness of lime plaster both indoors and outdoors) with high moisture buffering and small window area (36 m^2 i.e. 6 windows of 2 m x 3 m). This building has been chosen as representative to show an exemplary set of maps available in the CfC project database.

Within the "Climate for Culture" project it has been calculated how the above risk will likely change under the Representative Concentration Pathway (RCP) 4.5 Emission Scenario (van Vuuren et al., 2011) in the far future (2071-2100; Figure 6). The RCP 4.5 Scenario is based on long-term, global emissions of greenhouse gases, short-lived species, and land-use-land-cover which stabilizes radiative forcing at 4.5 watts per square meter (approximately 650 ppm CO2 equivalent) in the year 2100 without ever exceeding that value (Stocker et al., 2014).

The concept of historic climate is fundamental when the mechanical stress condition may be dominant over other deterioration mechanisms, e.g. pest infestation, hydrolysis, corrosion, and mineral transitions, as we will see later. Concerning other materials, e.g., metals and minerals, the concept of historic climate is also useful, but then as a reference to which the past, the present-day situation, and future scenarios may be compared (Camuffo et al., 2014; Bertolin et al., 2015). As recommended by the World Climate Programme (WCP) of the World Meteorological Organization (WMO), reference is made to a 30-yr period, at the present 1961-1990, and the difference between a future average situation and the average in the reference period is called “anomaly”. The anomaly is a useful index to individuate trends and be prepared to undertake mitigation measures.

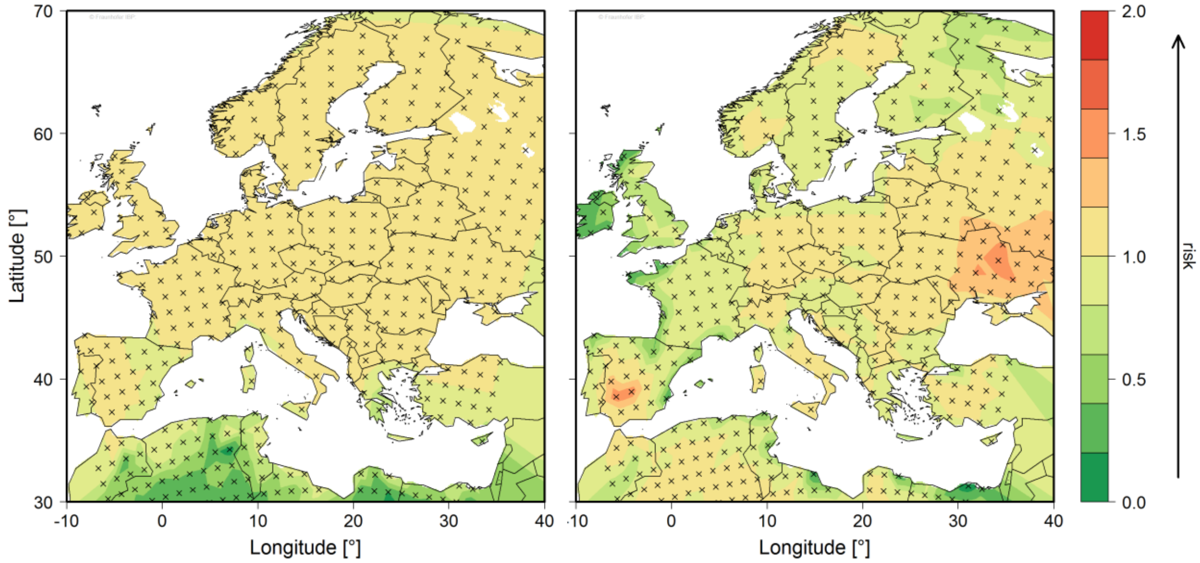

Figure 6 - Microclimate risk assessment for a wooden sculpture (left side) and a panel painting (right side) kept in an unconditioned building type 02 of the Climate for Culture Project. The simulation refers to the 2071-2100 far future RCP4.5 emission scenario. Risk increases from green (no risk) to yellow (alert) and red (risk)

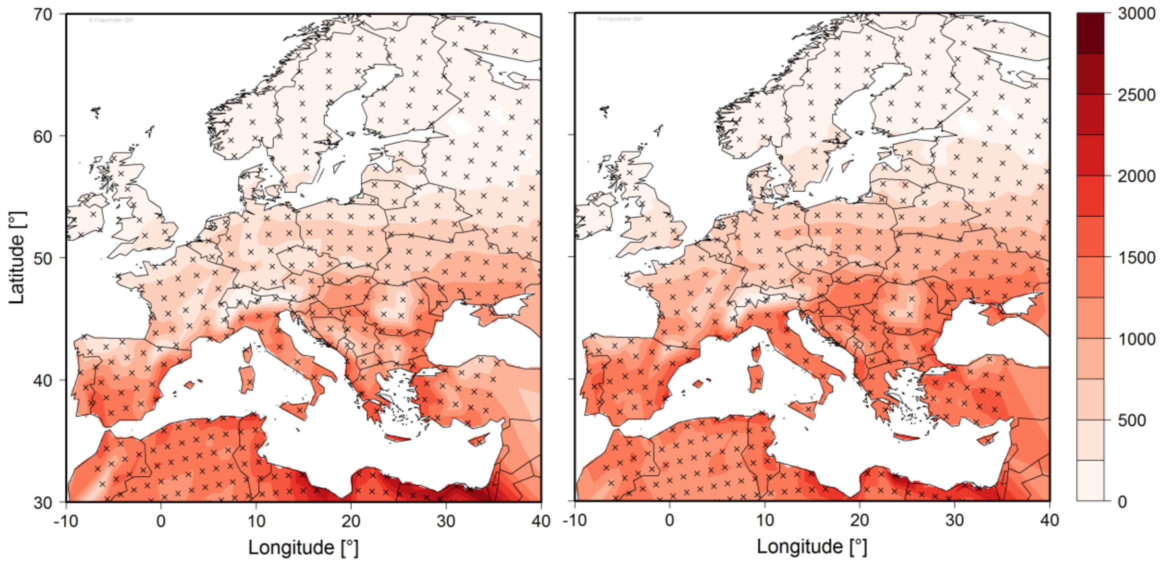

Figure 7 - Risk assessment for infestation of humidity dependent insects in an unconditioned building type 02 of the Climate for Culture Project. The simulations refer to the 1961-1990 reference past (left side) and 2071-2100 far future (right side) under the RCP4.5 emission scenario. Risk increases from white (no risk) to red (risk). Unit: growing degree day per year.

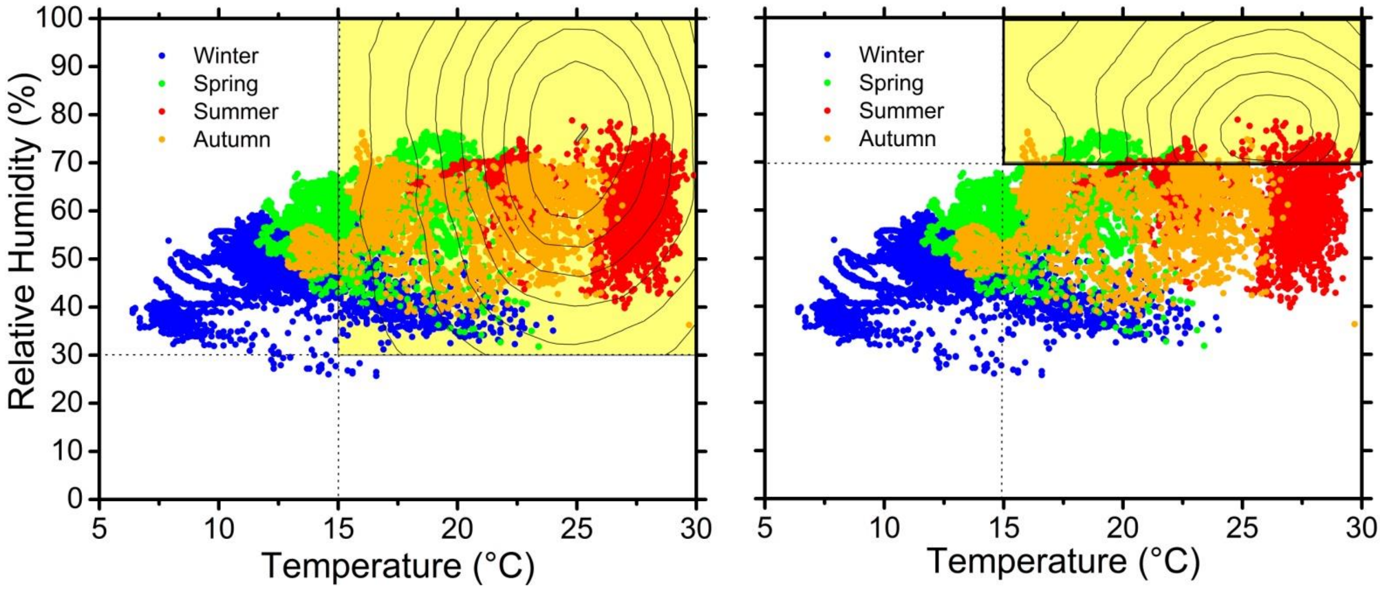

Figure 8 - Example of microclimate risk assessment tool for infestation of humidity resistant insects (left side) and humidity dependent (right side) insects. Color dots refer to RH readings in spring (green), summer (red), autumn (orange), and winter (blue). The yellow area refers to risk conditions.

INSECT INFESTATION

Furnishing in historic buildings and especially natural history collections and ethnographic museums that contain a large number of vulnerable organic exhibits are at a very high risk of pest infestation and damage (Querner, 2015). Pests are organisms that interfere with the management objective of the site. Pests come in a variety of forms: insects, rodents, bats, birds, and mold. Insects need comfortable conditions of T and RH, especially humid to damp environments that constitute a favorable habitat for eggs, larvae, and mature insects (Brimblecombe & Lankester, 2013; Child, 2013). At low T and/or RH they enter a comatose status for cold or dehydration. Under mild and humid conditions in the range 13°<T<35°C and 50<RH<100% the insects develop a certain activity that becomes particularly intense in the range 18°<T<24°C and 70<RH<100%. In this particularly favorable habitat, they may repeatedly deposit eggs and multiply. An index used in agriculture is given in terms of growing-degree-days (GDD) that are a measure of heat accumulation (i.e. the sum (Σ) of the degrees that exceed the 15°C threshold) to predict pest development rates and plan the use of pesticides (Herms, 2013) according to the formula

$$GDD = \Sigma(T-15°C)$$

when RH>70% and 15°<T<30°C. The yearly average of GDD for the 1961-1990 recent past and the simulation for 2071-2100 under the RCP4.5 emission scenario (van Vuuren et al., 2011) is shown in Figure 7.

A useful tool to assess the pest infestation risk in an exhibition room is to plot the matched pair of T and RH readings on a plot where the well-being or negative areas for insects are highlighted, as shown in Figure 8.

In this example, winter and most of spring are too arid for woodworms (*Anobium punctatum*); the most critical seasons being autumn and summer, as shown on the right diagram in Figure 8.

Some other insects, e.g. clothes moth (*Tineola bisselliella*) and drugstore beetle (*Stegobium Paniceum*) are more resistant to dryness (Brimblecombe et al., 2013), and their area of activity is found in the T and RH interval: T>15°C & RH>30%, as shown on the left side in Figure 8.

In another example shown in Figure 9, the yearly average of GDD is calculated as above, but under the condition that RH>30% and 15°<T<30°C. The GDD has been calculated for the 1961-1990 recent past and simulated for 2071-2100 far future under the RCP4.5 emission scenario (van Vuuren et al., 2011).

Insects die in very dry conditions (they dehydrate) or at very high temperatures. High temperatures, i.e. T>50-55°C for more than 10 minutes are lethal for insects and eggs (Strang, 1995; Lewis et al., 2000). A heat treatment is based on keeping objects in warm environments (e.g. a kiln or hot air) but this

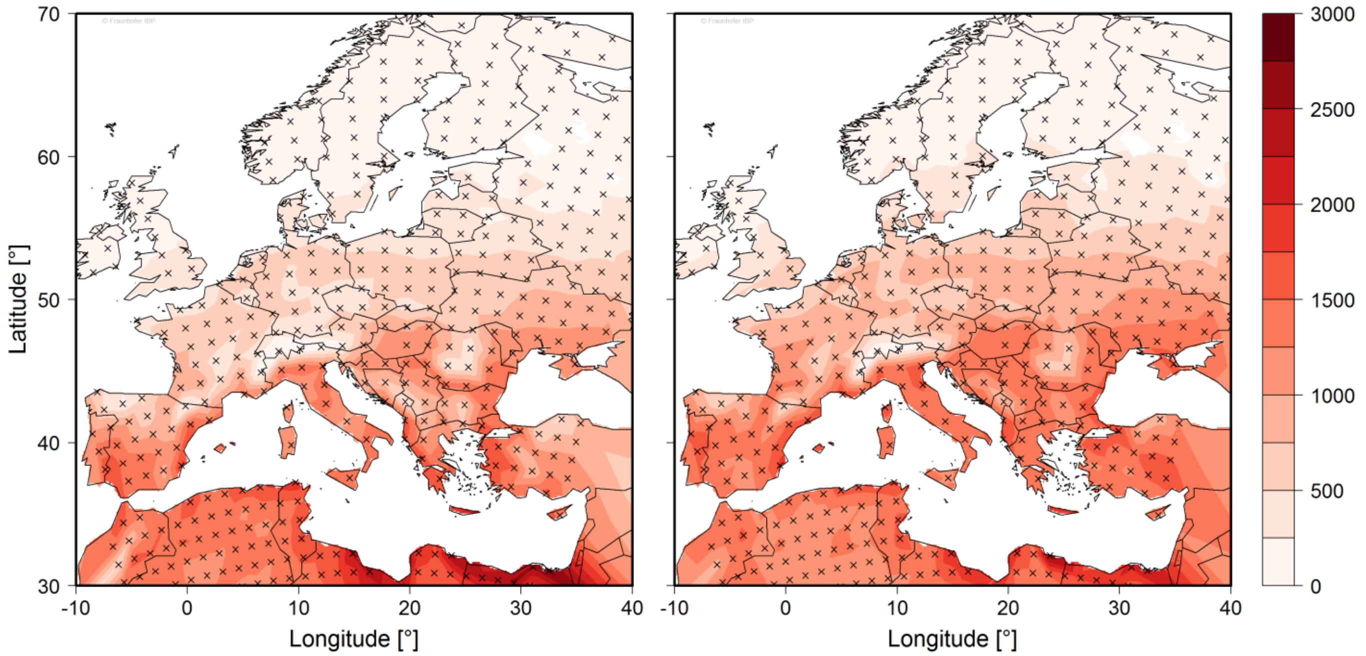

Figure 9 - Risk assessment for infestation of humidity resistant insects in an unconditioned building type 02 of the Climate for Culture Project. The simulations refer to the 1961-1990 reference past (left side) and 2071-2100 far future (right side) under the RCP4.5 emission scenario. Risk increases from white (no risk) to red (risk). Unit: growing degree day per year

method has three limiting factors, i.e. the time needed for heat to penetrate inside the object, the moisture gradients created inside the object, and the need for probes inserted inside the material to control the material temperature. Heating chambers have been developed to control the moisture content during the heating and cooling phase (Ackery et al., 2005). Dielectric heating which covers both radio frequency (RF) and microwave (MW) has been investigated for insect control in various materials, especially food (Pelletier and Colpitts, 2001; Das et al., 2013) and in the case of wooden collections (Bini et al., 1997; Olmi et al., 2009). The method is based on the consideration that the dielectric properties and the moisture content in insects, larvae, and eggs is greater than that in wood: this means that pests may be killed while wood remains at lower, non-dangerous temperatures. The main advantage is that the method is potentially appropriate for quick and high-volume treatments. However, if an object contains metallic inclusions, this may cause excess heating. Microwaving as a heat treatment may be risky, and for this reason it is not generally recommended (Strang and Kigawa, 2009).

Low temperatures, e.g. -20°C from 3 days to 1 week may be sufficient to kill adult insects as well as their eggs (Strang, 1997). However, the drop in temperature must be fast; if the change is slow, insects may adapt to the cold environment with various strategies (e.g. entering a hibernation-like state generating a variety of cryoprotectant molecules, with controlled freezing of the body fluids; Danks, 2006). No single treatment method may guarantee full success, and the best method applied has to be selected depending on the time, financial recourses, and availability and type of pests and materials to treat (Querner and Kjerulff, 2013). It may be that repeated cycles, a more extreme temperature, or longer exposures are needed to kill all pests. After treatment, objects should slowly acclimate to the room temperature, e.g. from one day to one week, in order to avoid mechanical damage.

Vacuum cleaners constitute an efficient way to kill small household pests (e.g. insects, spiders). Almost 95% of adult pests and their eggs are killed when sucked up with a powerful vacuum cleaner, because of the fan rotation (grinding insects), low pressure (exploding insects), and dehydration.

MOLD INFESTATION

The germination of sporae of various mold species requires a favorable habitat defined within certain intervals of T and RH (Macedo et al., 2009; Piñar and Sterflinger, 2009; Steiger et al., 2011). Laboratory tests have followed the critical conditions for a number of mold species, and the result has been plotted in a diagram that separates two areas: the safe

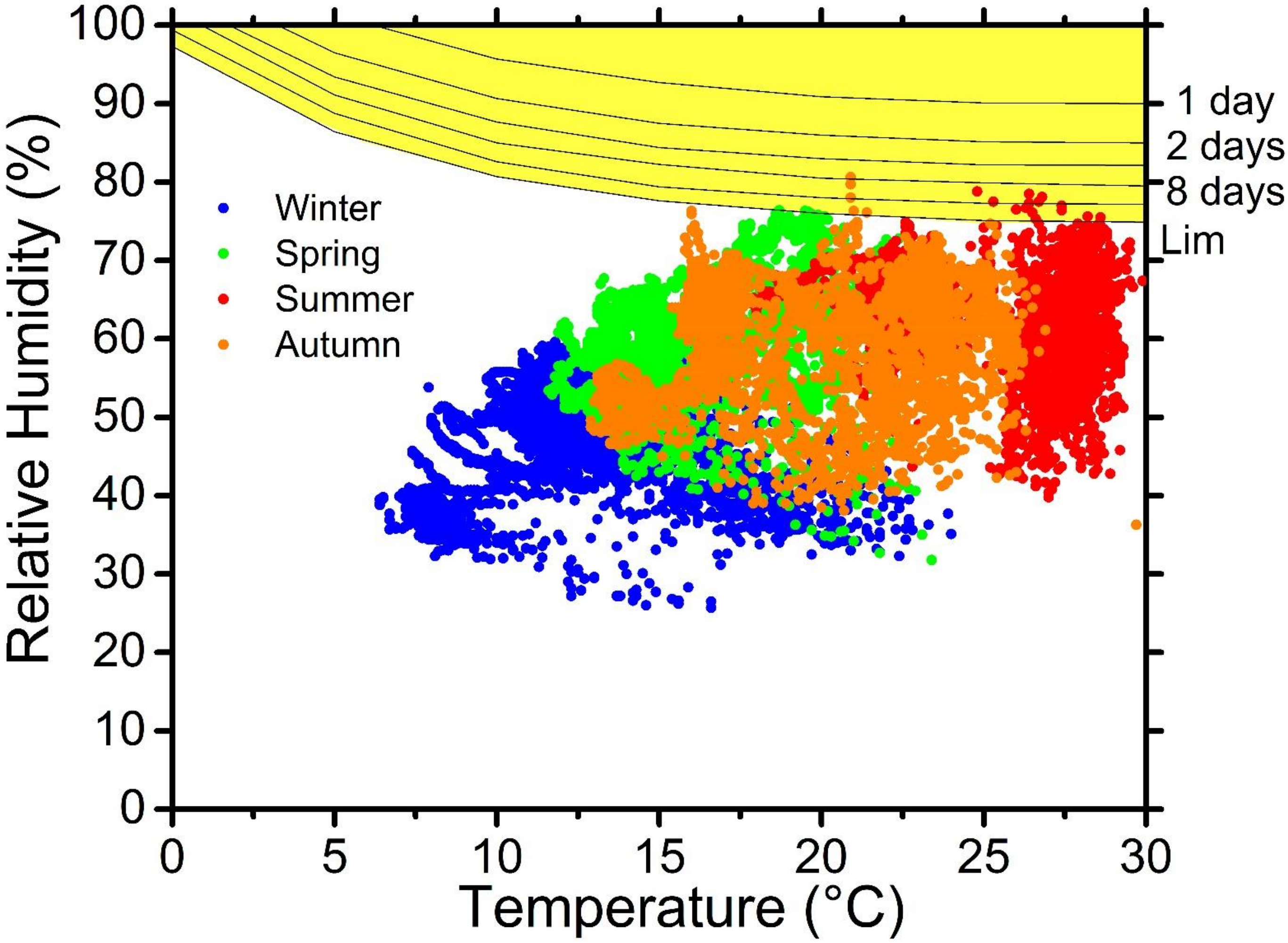

Figure 10 - Example of microclimate risk assessment tool for mold infestation. Color dots refer to RH readings in spring (green), summer (red), autumn (orange), and winter (blue). The yellow area refers to risk conditions.

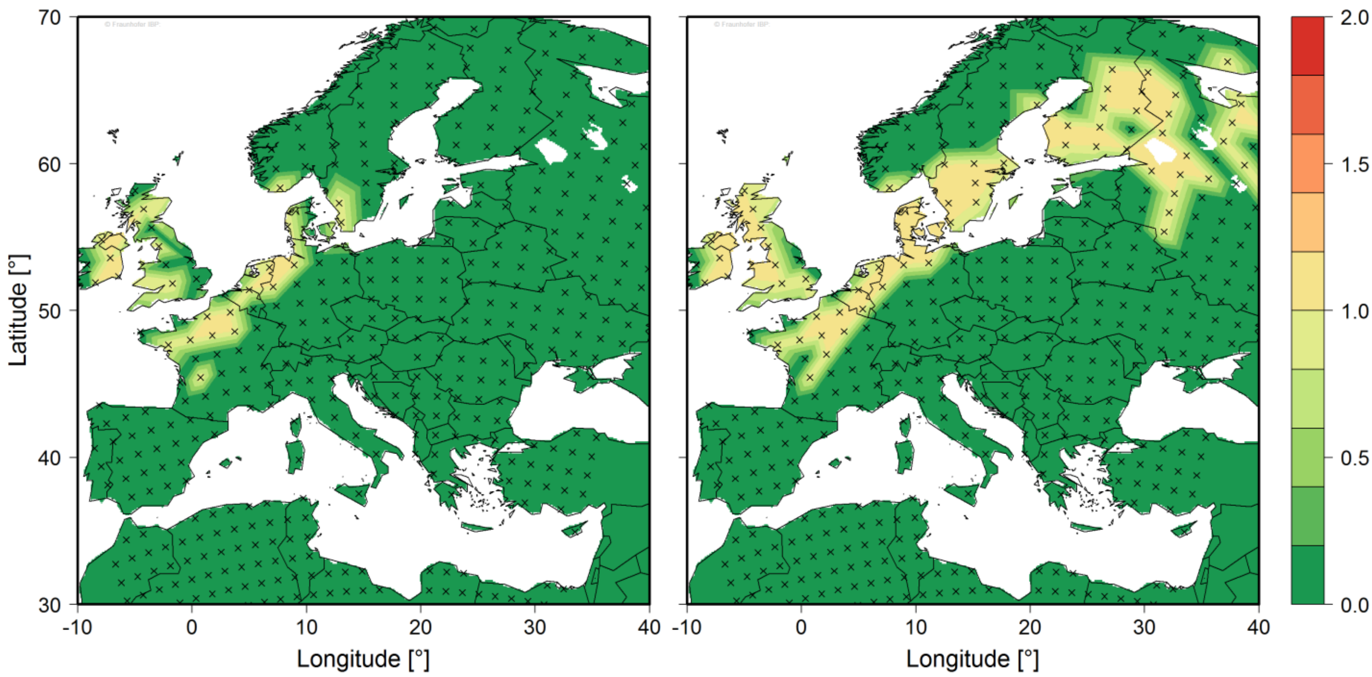

Figure 11 - Risk assessment for mold infestation in an unconditioned building type 02 of the Climate for Culture Project. The simulations refer to the 1961-1990 reference past (left side) and 2071-2100 far future (right side) under the RCP4.5 emission scenario. Risk increases from green (no risk) to yellow (alert) and red (risk).

area where molds cannot live and the risk area where mold may germinate after one or more days (Sedlbauer, 2002; Sedlbauer et al., 2011). Plotting the matched pairs of T and RH readings on the mold diagram (Figure 10) makes it possible to know whether a room is at risk of infestation or not. When RH>75% at mild temperatures, mold infestation and rotting are very likely to occur. There is no risk for RH<75% or for very low temperatures.

The above diagram is also useful to calculate future trends under the RCP4.5 emission scenario, e.g. comparing the 1961-1990 recent past with the simulation for 2071-2100 far future, as shown in Figure 11.

As for insects, temperature may be used for mold control. High temperatures, e.g. T >60°C, can be used to kill molds. Low temperatures (below freezing point) do not constitute an equally efficient way, especially if the temperature decreases at slow rate. In particular, the efficiency of the method increases with the water content in molds and sporae and the ice crystals that may form inside. Dry molds and sporae may survive in extreme conditions and become active again when the conditions improve.

CONSERVATION OF CELLULOSE

Organic fibers that form paper and some categories of textiles are largely composed of cellulose chains. Especially in damp environments and at high ambient temperatures, the cellulose chain may break down through hydrolysis, which leads to ageing and weakening of the paper or the textile. The rate constant of the hydrolysis reaction is described by the Arrhenius equation:

$$k = A \exp [-E_a/RT(K)]$$

where k is the so-called rate constant; A is a factor dependent on the number of molecular collisions in the system; E_a the activation energy; R the universal gas constant and T(K) the absolute temperature in Kelvin.

The degradation rate increases with increasing temperature (i.e. more energy available for the chemical reaction) and relative humidity (i.e. higher amount of moisture content in the hygroscopic material). In a T, RH diagram it is possible to calculate lines of equal degradation rate (called isoburns) or equal durability (called isoperms; Sebera, 1994).

Any increase in the reaction rate means a decrease in the lifetime of the paper or the textile. The lifetime is evaluated in terms of the so-called "lifetime multiplier" (LM):

$$LM = \left(\frac{50}{RH}\right)^{1.3} \; exp \frac{E_a}{R}\left(\frac{1}{T(K)} - \frac{1}{293}\right)$$

This parameter indicates how much at certain T and RH conditions the lifetime becomes longer (e.g. 10, 100, 1000 times) or shorter in comparison with the reference value LM=1 that has been assumed for T=20°C=293K and RH=50% (Michalski, 2002; Tétreault, 2003). One can evaluate the advantage of lowering either T or RH, or both, in a storage room by calculating the increase in lifetime. The cost of the new climate control should be always assessed.

As an example, lowering T by 5°C will double the lifetime, and halving RH will more than double the lifetime (Michalski, 2002). However, one should be reminded that this holds for the chemical degradation of the cellulose molecule, but lowering RH may irreversibly damage wooden objects that will likely undergo deformation or fracturing.

EXHIBITION LIGHTING

Light is necessary for the enjoyment of exhibits, but it is responsible for a number of deterioration mechanisms, e.g. color fading, photochemical degradation of vulnerable materials, object overheating and dehydrating, colonization of phototropic organisms, air motions, and deposition of airborne pollutants (Bacci and Cucci, 2010; Camuffo, 2013). In order to minimize the above negative effects, a careful choice and use should be made of light sources and filters.

The EU normative for lighting cultural heritage collections is based on two standards: CIE 157:2004 "Control of damage to museum objects by optical radiation" and CEN TS 16163: 2014 "Conservation of cultural heritage - Guidelines and procedures for choosing appropriate lighting for indoor exhibitions". They constitute a frame that specifies light sources, lighting risks to cultural heritage, and recommended practices to reduce risk of damage to collections.

The photochemical risk depends on the vulnerability of the exhibits. For most photosensitive exhibits, damage is caused by the quantity of light (luminous exposure, i.e. product of intensity and duration) and its spectral distribution. The damage increases exponentially with the photon energy, i.e. inversely to wavelength, therefore, spectral ranges of the radiation can be ordered according to the decreasing degradation potential: ultraviolet (UV), followed by violet, blue etc. To this aim, materials are classified in four classes of sensitivity to photochemical deterioration mechanisms, as follows:

Class 1, no sensitivity: most metals, stone, most glass, ceramic, enamel, most minerals

Class 2, low sensitivity: most oil and tempera painting, fresco, un-dyed leather and wood, horn, bone, ivory, lacquer, some plastics

Class 3, medium sensitivity: most textiles, watercolors, pastels, prints and drawings, manuscripts, miniatures, paintings in distemper media, wallpaper, and most natural history exhibits, including botanical specimens, fur and feathers

Class 4, high sensitivity: silk, highly fugitive colorants (vegetal or animal origin), most graphic art and photographic documents.

Exhibition requires an appropriate compromise between enjoyment and deterioration. This means to limit either the lighting intensity or the illumination time or both. Lighting levels much below 50 lux will result in poor viewing conditions and loss of perception of color and surface details. This is particularly relevant for aged visitors whose perception threshold is much higher (e.g. a 60 year old person needs twice the light level of a 20 year old person). The museum directors may choose to increase the luminance level (lux), but with a correspondent decrease in the exposure time (hours). They should respect the product

$$L \times ET = ALE$$

where L is luminance (lux), ET the exposure time (hours) and ALE (lux hr) the upper limit of the annual luminous exposure that depends on the photosensibility of each material and shall comply with the limiting values specified as follows:

Class 1, no sensibility: no limit of annual exposure time (hr) and illuminance intensity (lux).

Class 2, low sensitivity: upper limit of annual luminous exposure: 600,000 lux hr derived from the reference values of 3,000 hr annual exposure time (i.e. 10 hours per day, multiplied by 300 working days) and 200 lux illuminance intensity.

Class 3, medium sensitivity: upper limit of annual luminous exposure: 150,000 lux hr derived from the reference values of 3,000 hr annual exposure time and 50 lux illuminance intensity. It is possible, however, to increase the illuminance intensity for a better enjoyment but decrease the time duration accordingly.

Class 4, high sensitivity: upper limit of annual luminous exposure: 15,000 lux hr derived from the reference values of 300 hr annual exposure time and 50 lux illuminance intensity. In this class, due to the high vulnerability of exhibits, the annual exposure time has been reduced 10 times.

Lamp Types

Various types of lamps exist, e.g. incandescent, fluorescent, metal halides, LED. The most popular lamps for exhibition purposes are halogen and LED lamps.

Halogen lamps have a color temperature from 3000 to 4000 K with a continuous light spectrum, and the human perception of an object illuminated by such a source is similar to that of the object illuminated by sunlight. This means that the halogen lamp has an excellent Color Rendering Index (Ra = 100). However, the emitted light spectrum includes IR that overheats the lighted exhibits as well as the room.

Warm white LED, with a color temperature around 3000 K, has a lower Color Rendering Index i.e. Ra = 80-90, but generally it does not produce heat in the form of infrared (IR) emission added to the light beam. The blue peak may be simply cut off with a yellow filter, as suggested by CEN TS 16163: 2014. Alternatively, the LED spectrum may be improved to approach the solar spectrum by adding a well-balanced number of colored LEDs (red, green, cyan, and violet) to the basic array composed of many warm white LEDs, to compensate for the reduced spectral intensities in comparison with the solar light. The blue peak of the white warm LED may be reduced with the addition of the complementary yellow light. A well balanced light requires expertise and laboratory tests but provides good results, as documented by recent changes to the lighting in the Sistine Chapel, Rome (Bogani, 2015; Camuffo, 2015).

MUSEUM SHOWCASES

The EU standard EN 15999-1: 2014 constitutes a guideline for design of showcases for exhibition and preservation of objects. It provides general instructions to assess the main purposes of a showcase, i.e.: (i) to reduce the risk of physical damage to exhibits (e.g. theft, vandalism, and natural disasters) and (ii) to improve the control of environmental parameters (e.g. relative humidity, air temperature, dust, pollutants, and light).

The standard specifies the characteristics and the conditions for use of showcases for safe and secure display of exhibits. Part 1: "General instructions" was approved in 2014; Part 2: "Technical aspects" is under discussion. Part 1 specifies the principles which should be considered when designing or selecting a showcase, i.e.:

- Functions of the showcase
- Criteria for design or selection of a showcase
- Components of the showcase
- Security and safety
- Construction materials, assembly, and fixing
- Management of the environmental conditions (microclimate, lighting, pollutants, dust and microorganisms)
- Location, use, and maintenance of the showcase

The standard poses the question: what is the best showcase? The concept of "*best*" is relative and will change with your purposes and your exhibit. The best showcase is simply the one that best fits the user's conservation and exhibition needs. You should know what you need, and consequently choose your showcase. The standard may assist in improving awareness and choice. Thresholds, levels, and specifications will be considered in Part 2 of the standard (at present under development at CEN TC 346).

Volatile organic compounds (VOC) outgassing from materials constitute a risk for conservation (Tétreault, et al., 2003; 2013). Wooden showcases constitute a potential risk factor for the emission of VOC, especially acetic and formic acids that are naturally released by wood, e.g. oak, walnut, pine, poplar, listed in order of outgassing severity. The outgassed VOC remains entrapped in the showcase volume and will corrode metal exhibits, paper, textiles, and other vulnerable materials. VOC may be released by polyvinyl acetate (PVAc) and varnishes that constitute an important risk factor for exhibits.

CONCLUSIONS AND RESEARCH NEEDS

The key questions considered in this paper are: Do optimal intervals of T, RH exist for the conservation of collections? Is it really necessary to keep constant T and RH? Can we assess a tolerable range of departures from the average levels of T, RH? Can we assess thresholds for safe conditions and risk identifications?

Microclimate is continually variable over space and over time. Careful controls and regular monitoring are necessary to timely recognize unfavorable conditions in exhibition rooms. Early detection, the use of risk assessment tools, and the adoption of preventive conservation measures are prerequisites necessary to preserve collections. It has been demonstrated that avoiding harmful conditions that depend on the material type does not necessarily require high costs for expensive HVAC systems.

The focus should be clear: the best possible preservation conditions for the collections. If one is concerned about shrinkage/swelling, condensation/ evaporation, corrosion, pest infestation, or any other deterioration mechanism, one should not be interested in what is happening in the air, maybe in the middle of the room, but rather in what is happening on the surface of the individual exhibits and how exhibits interact with the air.

Harmful conditions and recommendable T, RH intervals change with the material type and the deterioration mechanism. A list of recommendations and risk assessment tools are available today, but further research is still necessary, as follows.

Organic hygroscopic materials have been adapted to the previous climate conditions, i.e. the historic climate, and are particularly vulnerable to mechanical damage. For this reason the EU standard EN 15757:2010 recommends to stay within the 7th and 93rd percentiles of the RH fluctuations of the historic climate if this has proven to be satisfactory for the preservation.

Specific tools in the T, RH domain have been developed to investigate whether an environment is safe or harmful for wooden objects or polychromies. However, mechanical stress is a major, but not the only one deterioration mechanism. In addition, when aged wood has been attacked by insects or molds, it changes its mechanical characteristics depending on the severity of the attack. The COST Action IE0601 has considered the ageing processes, their factors (physical, mechanical, biological, chemical, and environmental), and their interactions in order to improve the conservation of wooden artworks (Gril, 2012). However, the change of mechanical properties of wood attacked by pests is still unknown and needs further research.

Organic hygroscopic materials may also be affected by pests, e.g. insect or mold attack. Insects and molds find a favorable habitat and develop when mild temperatures occur at the same time as high humidity levels (e.g. RH>70%). Specific tools in the T, RH domain have been developed to investigate whether an environment is safe or harmful for insect or mold infestation. The harmful conditions should be avoided whenever possible. The final environmental variability range may be a compromise between the historic climate and environmental conditions unfavorable to pests. Should this occur, a study should be made to decide the best strategy, e.g. whether it is preferable to change climate conditions or use pesticides. It is clear that pesticides are poisonous and noxious to man and the environment. However, the thermal treatments to kill insects or molds are not easy and might damage collections. In fact, while low-temperature treatment remains the most popular solution when ethnographic artefacts are actively infested, the need for preventive low-temperature exposure for objects entering and re-entering the museum environment (e.g. after loans or several relocations and/or treatments) is less obvious. Museum staff must weigh the potential risk for devastating loss through insect damage against the possible cumulative damage posed by repeated low-temperature exposure (Carrlee, 2003).

For cellulose, the best preservation is with low T and RH levels. This is a general condition to reduce chemical reactions, in accordance with the Arrhenius equation, i.e. to reduce the rate at which the hydrolysis occurs and to increase the lifetime of paper and textiles. However, the life of the cellulose molecule is not the only problem met by textiles or books. The conclusion is that chemical degradation is only one among several factors of degradation that should be considered in a conservation plan, some of them with conflicting needs. In practice, we may know the different strategies, but we still have a poor knowledge about their synergism and how to minimize drawbacks.

Exhibition lighting may have a number of harmful consequences, especially for photosensitive surfaces, and is regulated by CIE 157:2004 and CEN TS 16163: 2014. Another noxious effect in damp underground environments is the colonization of algae or molds. To this aim the use of lamps emitting wavelengths not utilized by phototrophic organisms is recommended. However, the infesting species may change over time for a number of reasons (e.g. exchanges with the exterior, adaptation), and this requires a continual control of the mold species and lighting strategy.

Finally, showcases provide closed environments, often considered the best for conservation purposes. However, they may release and keep VOC, or may constitute a convenient habitat for microbial colonization, or become a small greenhouse. EN 15999-1: 2014 is a useful guideline for design of showcases to the aims of exhibition and preservation of collections. The Part 2 of this standard, focused on technical aspects, is still under development at CEN.

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REFERENCES CITED

Ackery, P., D. Pinniger, A. Doyle, and K. Roux. 2005. Heat treatment of entomological drawers using the thermo lignum heat process. Collection Forum 19:15–22.

ASHRAE. 2003. Museums, libraries, and archives; pp. 21.1-21.16 in ASHRAE Handbook - Heating, Ventilating, and Air-Conditioning Applications. American Society of Heating, Refrigeration and air-Conditioning Engineers, ASHRAE, Atlanta, Georgia, USA.

ASHRAE. 2007. Museums, libraries and archives; pp. 21.1-21.23 in ASHRAE Handbook - Heating, Ventilating, and Air-Conditioning Applications. American Society of Heating, Refrigeration and air-Conditioning Engineers, ASHRAE, Atlanta, Georgia, USA.

Bacci, M., and C. Cucci. 2010. The role of light; pp. 59–68 in D. Camuffo, V. Fassina, and J. Havermans (eds.), Basic Environmental Mechanisms Affecting Cultural Heritage - Understanding Deterioration Mechanisms for Conservation Purposes. Nardini, Florence, Italy.

Bertolin, C., D. Camuffo, and I. Bighignoli. 2015. Past reconstruction and future forecast of domains of indoor relative humidity fluctuations calculated according to EN 15757:2010. Energy and Buildings 102:197–206.

Bini, M., D. Andreuccetti, A. Ignesti, R. Olmi, S. Priori, and R. Vanni. 1997. A portable microwave system for woodworm disinfestation of artistic painted boards. Journal of Microwave Power and Electromagnetic Energy 32:180–187.

Bogani, C. M. 2015. A digital integrated lighting system. Study and project; pp. 279–289 in A. Paolucci and V. Cimino (eds.), The Sistine Chapel twenty years later. New breath new light. Proceedings of the International Conference 30-31 October 2014. Vatican Museums, Vatican City State, Italy.

Bratasz, L. 2010. Acceptable and non-acceptable microclimate variability: the case of wood; pp. 49–58 in D. Camuffo, V. Fassina, and J. Havermans (eds.), Basic environmental mechanisms affecting cultural heritage. Understanding deterioration mechanisms for conservation process. vol. 42. Nardini, Florence, Italy.

Bratasz, Ł., R. Kozłowski, D. Camuffo, and E. Pagan. 2007. Impact of indoor heating on painted wood. Monitoring the altarpiece in the church of Santa Maria Maddalena in Rocca Pietore, Italy. Studies in Conservation 52:199–210.

Brimblecombe, P., and P. Lankester. 2013. Long-term changes in climate and insect damage in historic houses. Studies in Conservation 58:13–22.

Brimblecombe, P., C. T. Brimblecombe, D. Thickett, and D. Lauder. 2013. Statistics of insect catch within historic properties. Heritage Science 1:34.

Camuffo, D. 2010. The role of temperature and moisture; pp. 1–30 in Basic Environmental Mechanisms Affecting Cultural Heritage - Understanding Deterioration Mechanisms for Conservation Purposes. Nardini, Florence, Italy.

Camuffo, D. 2013. Microclimate for Cultural Heritage: Conservation, Restoration, and Maintenance of Indoor and Outdoor Monuments. Elsevier, New York, USA, 557 pp.

Camuffo, D. 2015. A special restoration site, the memory of Dario Camuffo; pp. 53–63 in A. Paolucci and V. Cimino (eds.), The Sistine Chapel twenty years later. New breath new light. Proceedings of the International Conference, 30-31 October 2014. Vatican Museums, Vatican City State, Italy.

Camuffo, D., C. Bertolin, A. Bonazzi, F. Campana, and C. Merlo. 2014. Past, present and future effects of climate change on a wooden inlay bookcase cabinet: A new methodology inspired by the novel European Standard EN 15757:2010. Journal of Cultural Heritage 15:26–35.

Carrlee, E. 2003. Does low-temperature pest management cause damage? Literature review and observational study of ethnographic artifacts. Journal of the American Institute for Conservation 42:141–166.

Child, R. 2013. The influence of the museum environment in controlling insect pests; pp. 419–424 in J. Ashley-Smith, A. Burmester, and M. Eibl (eds.), Climate for Collections-Standards and Uncertainties. Doerner Institut, München, Germany.

Danks, H. V. 2006. Insect adaptations to cold and changing environments. The Canadian Entomologist 138:1–23.

Das, I., G. Kumar, and N. G. Shah. 2013. Microwave heating as an alternative quarantine method for disinfestation of stored food grains. International Journal of Food Science 2013:e926468.

Gril, J. 2012. Wood science for conservation. Journal of Cultural Heritage 13:1–125.

Herms, D. A. 2013. Using degree-days and plant phenology to predict pest activity; pp. 49–59 in Tactics and Tools for IPM. The University of Minnesota, Minnesota, USA.

Lewis, V. R., A. B. Power, and M. I. Haverty. 2000. Laboratory evaluation of microwaves for control of the western drywood termite. Forest Products Journal 50:79–87.

Macedo, M. F., A. Z. Miller, A. Dionísio, and C. Saiz-Jimenez. 2009. Biodiversity of cyanobacteria and green algae on monuments in the Mediterranean Basin: an overview. Microbiology 155:3476–3490.

Martens, M., and H. Schellen. 2013. Climate risk assessment in museums; pp. 363–374 in J. Ashley-Smith, A. Burmester, and M. Eibl (eds.), Climate for Collections - Standards and Uncertainties. Doerner Institut, München, Germany.

Mecklenburg, M. F., C. S. Tumosa, and D. Erhardt. 1998. Structural response of painted wood surfaces to changes in ambient relative humidity; pp. 464–483 in V. Dorge and F. C. Howlett (eds.), Painted wood: history and conservation (Part 6: Scientific Research). Getty Conservation Institute, Los Angeles, USA.

Michalski, S. 2002. Double the life for each five-degree drop, more than double the life for each halving of relative humidity; pp. 66–72 in R. Vontobel (ed.), Preprints of 13th Meeting of ICOM-CC. Earthscan, London, UK.

Michalski, S. 2009. The ideal climate, risk management, the ASHRAE chapter, proofed fluctuations, and towards a full risk analysis model; pp. 1–19 in Contribution to the Experts' Roundtable on Sustainable Climate Management Strategies, held in April 2007, in Tenerife, Spain. Getty Conservation Institute, Los Angeles, USA.

Olmi, R., M. Bini, A. Ignesti, S. Priori, C. Riminesi, D. Pinna, and P. Tiano. 2009. Development of innovative microwave applicators for the treatment of biodeteriogens and biotic agents in artistic/archaeological contexts. Proceedings of 12th International Conference on Microwave and High Frequency Heating: 25-28.

Pelletier, Y., and B. G. Colpitts. 2001. The use of microwaves for insect control; pp. 125–133 in D. C. Vincent, D. B. Panneton, and D. F. Fleurat-Lessard (eds.), Physical Control Methods in Plant Protection. Springer Berlin Heidelberg.

Piñar, G., and K. Sterflinger. 2009. Microbes and building materials; pp. 978–1 in D. N. Cornejo and J. L. Haro (eds.), New building materials: properties, performance and applications. Nova Science Publishers, Inc., New York, USA.

Querner, P. 2015. Insect pests and Integrated Pest Management in Museums, Libraries and Historic Buildings. Insects 6:595–607.

Querner, P., and A. K. Kjerulff. 2013. Non-chemical methods to control pests in museums: An overview; pp. 273–276 in M. A. Rogerio-Candelera, M. Lazzari, and E. Cano (eds.), Science and Technology for the Conservation of Cultural Heritage. Taylor & Francis, London, UK.

Sebera, D. K. 1994. Isoperms: An Environmental Management Tool. Commission on Preservation and Access, Washington, DC, USA, 16 pp.

Sedlbauer, K. 2002. Prediction of mould growth by hygrothermal calculation. Journal of Building Physics 25:321–336.

Sedlbauer, K., W. Hofbauer, N. Krueger, F. Mayer, and K. Breuer. 2011. Material specific isopleth-systems as valuable tools for the assessment of the durability of building materials against mould infestation–The "isopleth-traffic light." International Conference on Building Materials and Components, Porto, Portugal 1–8.

Steiger, M., A. E. Charola, and K. Sterflinger. 2011. Weathering and Deterioration; pp. 227–316 in S. Siegesmund and R. Snethlage (eds.), Stone in Architecture. Springer, Berlin, Germany.

Stocker, T. F., D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley. 2014. Climate Change 2013: The Physical Science Basis. Cambridge University Press, Cambridge, UK, pp.

Strang, T. 1995. A brief guide to thermal and controlled atmosphere treatments for insect eradication. ICOM-CC Preventive Conservation Working Group Newsletter 4–5.

Strang, T. 1997. Controlling insect pests with low temperature. Canadian Conservation Institute Notes 3:1–4.

Strang, T., and R. Kigawa. 2009. Combatting pests of cultural property. Canadian Conservation Institute Technical Report 29:1–44.

Tétreault, J. 2003. Airborne Pollutants in Museums, Galleries, and Archives: Risk Assessment, Control Strategies, and Preservation Management. Canadian Conservation Institute, Ottawa, Canada, 168 pp.

Tétreault, J., A.-L. Dupont, P. Bégin, and S. Paris. 2013. The impact of volatile compounds released by paper on cellulose degradation in ambient hygrothermal conditions. Polymer Degradation and Stability 98:1827–1837.

Tétreault, J., E. Cano, M. van Bommel, D. Scott, M. Dennis, M.-G. Barthés-Labrousse, L. Minel, and L. Robbiola. 2003. Corrosion of copper and lead by formaldehyde, formic and acetic acid vapours. Studies in Conservation 48:237–250.

van Vuuren, D. P., J. Edmonds, M. Kainuma, K. Riahi, A. Thomson, K. Hibbard, G. C. Hurtt, T. Kram, V. Krey, J.-F. Lamarque, T. Masui, M. Meinshausen, N. Nakicenovic, S. J. Smith, and S. K. Rose. 2011. The representative concentration pathways: an overview. Climatic Change 109:5.

STANDARDS CITED

CEN TS 16163: 2014. Conservation of Cultural Heritage - Guidelines and procedures for choosing appropriate lighting for indoor exhibitions. European Committee for Standardization, Brussels, Belgium.

CIE 157: 2004. Control of Damage to Museum Objects by Optical Radiation. International Commission on Illumination, Vienna, Austria.

EN 15757: 2010. Conservation of Cultural Property - Specifications for temperature and relative humidity to limit climate-induced mechanical damage in organic hygroscopic materials. European Committee for Standardization, Brussels, Belgium.

EN 15759-1: 2011. Conservation of cultural property — Indoor climate – Part 1: Guidelines for heating churches, chapels and other places of worship. European Committee for Standardization, Brussels, Belgium.

EN 16242: 2012. Conservation of cultural heritage - Procedures and instruments for measuring humidity in the air and moisture exchanges between air and cultural property. European Committee for Standardization, Brussels, Belgium.

EN 15999-1: 2014. Conservation of cultural heritage. Guidelines for design of showcases for exhibition and preservation of objects. Part 1: General instructions. European Committee for Standardization, Brussels, Belgium.

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