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Ecofriendly Protection from Biofouling of the Monitoring System at Pantelleria's Cala Gadir Underwater Archaeological Site, Sicily

Gradually in recent years the emphasis in underwater archaeology has moved from excavation to preservation *in situ*, making sites accessible to divers through marked trails, and to non-divers via video links. In this context, Sicily's Superintendent of the Sea has, since 2002, at the Cala Gadir archaeological site off the coast of Pantelleria (Fig. 1), established a series of underwater cameras connected to the internet, called the Sistema Integrato per la Tutela dell'Archeologia Subacquea (STARS) (http://www.progettostars.it).

The archaeological site

By the mid-7th century BC Carthaginians occupied Pantelleria (and Malta) which, combined with long-established Phoenician settlements on Crete, Rhodes and Cyprus, gave them a set of stepping-stones back to their home port of Tyre (Casson, 1991). Named Gadir like the analogous Phoenician port in Spain now called Cadiz, the bay offers excellent natural shelter from all winds, except from the west. Furthermore, in the past the sea penetrated inland for an additional 200 m, making the landing place even safer (Chioffi, 2006).

Hundreds of amphoras, more or less covered in sand or mud, lie in the bay at depths varying from 27 to 42 m and within a radius of *c*.300 m. Since the early 1950s the site has been pillaged by divers. The first legal recovery and exploration dates back to 1972–73. Fortunately the trophy-seekers had only damaged the visible part of the cargoes. The amphoras so far recovered, Roman examples of the Dressel types 1A, 1B, 1C 2–6, Greco-Italic, and Punic of 12 different types are testimony to more than one ancient shipwreck dating back to the 4th century BC onwards. More recently, in 1998, new pieces of wood thought to be from a Phoenician wreck were found, and more than 300 amphoras recovered. In the summer of 2000 the Superintendent of the Sea continued to search for the hull of the ship which was carrying the amphoras. In collaboration with the Italian

Figure 1. Pantelleria's Gadir Bay is a natural harbour (top) intensively used as a port-of-call by Carthaginians.

military police, archaeologists started a systematic survey of the area, including in the deeper water with the help of ROV 'Pluto'. Altogether an area of *c*.40,000 m^2 was surveyed at depths of between 50 and 120 m.

The sea-bed is gently sloping, with many scattered amphoras clearly trending downwards from the actual wreck-site. During this survey archaeologists encountered both Punic and Italic amphoras (types: Mana C1, Mana C2, Greco-Italic, Dressel 1A1, 1A2, 1B, 1C, 2, 4, 18). As this material came from deep survey, it supported the idea that in Gadir we have more than one wreck and that the site is still worthy of investigation, even if we know that it has been damaged in the past by looters. Analysis of the amphoras led to the conclusion that the first shipwreck dates to the end of the 3rd or the first half of the 2nd century BC. This ship carried a mixed cargo of Phoenician (manufactured in Carthage) and late Italic amphoras used to transport wine. Indeed, many carry inscriptions with Punic letters, stamps or marks which provide useful information on the manufacturing site, the city of origin, the trader or even the content. The second wreck dates to the end of the 2nd or the beginning of the 1st century BC, with Italic amphoras of Dressel 1 and Lamboglia 2 types, manufactured in what is now Tunisia, and which were mostly used to hold food. Two hundred of these amphoras now form the centrepiece of an exhibition held every summer since 1998 in the Castle of Pantelleria (Tusa *et al.*, 2004).

The STARS project

Shortly after the 2000 discovery, the Superintendent of the Sea decided to create an underwater archaeological museum. Installation of a set of remotely-controllable cameras allows those who do not dive to visit the site, where a large lead anchor and several ancient amphoras lie partially buried in the sand 30 m below the surface. Two controllable cameras—one moving on a track within an acrylic-glass tube, and another freely rotatable within a protective plastic dome—are controlled through a web interface. By connecting to the website (www.progettostars.it) users can freely explore the site, as specific links enable the two cameras to be redirected at will. Ancient artefacts can be seen partially buried in the sand. The project was realized in collaboration with Italian company West End, and filmed by Italy's state television (broadcast October 2007, and still accessible online at http://www.lineablu.rai.it).

The system not only makes the archaeological heritage more accessible, but helps to protect it against theft, as the control system also operates at night thanks to a set of LED lamps, while an ultrasound pulse system, also located on the sea-bed, recognizes any possible intrusion onto the site. All signals are coded and sent to a control centre (CdC). In case of alarm, a signal (including the precise location of intrusion and an image of the site) is automatically sent to the police, who from their terminals can access the images sent by another camera, allowing accurate evaluation in order to decide about intervention.

Once control was in place, a set of underwater archaeological trails was successfully set up around Gadir, highlighting the two wreck-sites, where divers can view the ancient finds *in situ*, at depths of 18–30 m. The visitor can appreciate the scale of what was in the past a frequently-used anchorage. Laminated guides have been created in order to make the visits easier for underwater tourists.

Antifouling protection

However, to keep working the system needs protection against marine biofouling (Flemming, nd). Otherwise, settlement of a biofilm and subsequent proliferation of marine organisms will rapidly cover the external surface of the monitoring device, requiring expensive mechanical cleaning which also inevitably disturbs a fragile archaeological site. However, the use of a new, ecofriendly antifouling coating trade-named Aquafast (Tang *et al.*, 2005) actually minimizes biofilm formation over at least a 9-month period. This is important, as pollution of the sea due to traditional antifouling paints is a serious global environmental problem (Borghi and Porte, 2002), whereas ecofriendly protection such as that described here not only prevents marine pollution in a delicate environment, but also saves financial resources which can be invested in useful activities such as further archaeological research.

The coating is easy to produce, robust, and uses critical surface-tension amongst other physico-chemical characteristics to create a barrier to prevent marine species from getting established. Trademarked AquaFast, this non-biocidal commercial antifouling product has been recently developed by researchers at the State University of New York at Buffalo, with grant support from the US Office of Naval Research (Detty *et al.*, 2007). The coating solution is transparent, prepared from

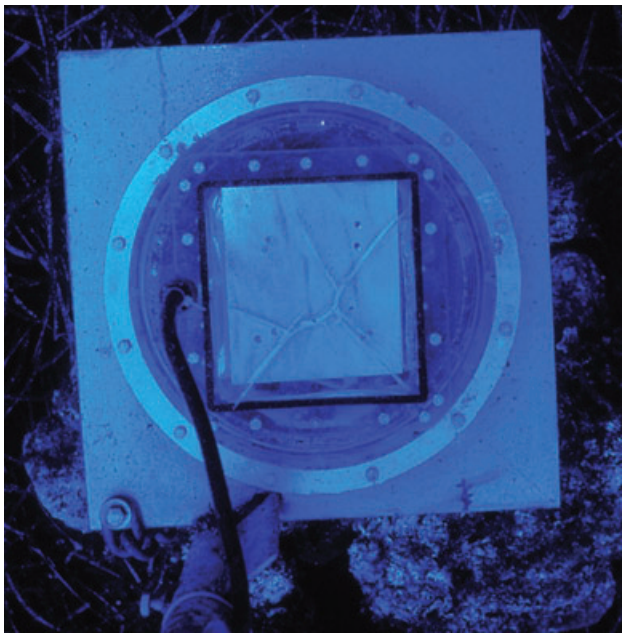

Figure 2. Photograph of the camera at 30 m below the surface on the Cala Gadir site.

an equimolar mixture of tetraethoxysilane (TEOS) and n-octyltriethoxysilane (C8-TEOS) in isopropanol and water which has undergone hydrolysis and condensation catalyzed by a catalytic amount of HCl. The reagents are magnetically stirred under ambient conditions for 2 h, and then capped in aluminium bottles.

The sol is easily applied by brushing. The resulting transparent layer cures rapidly at room temperature to provide the final dry gel (xerogel) surface. The physicochemical properties of the transparent glassy layer made of organically modified silicate (ORMOSIL) minimize adhesion of marine species to the coated surface, providing a surface that is recognized as 'inhospitable' to settlement by marine organisms. Fig. 2 shows the camera protected by the methacrylate dome 30 m deep in Cala Gadir. The plate and the tube supporting the camera were coated with an AquaFast layer in August 2007 and the system was recovered in May 2008. As shown in Fig. 3, little biofouling is observed on either the tube or the plate, whereas the bottom of the plate, which was not treated, is covered by thick spots of biological incrustation.

For fouling to occur, the surface must have favourable characteristics for organisms both to settle and adhere. The natural glues which hold the organisms to exposed surfaces must compete with the surrounding water. There is a zone of minimal bioadhesion which is related to critical surface tension, γ_C. Comprehensive contact-angle analysis

Figure 3. The camera dome and support system after 8 months of continuous deployment underwater at Cala Gadir. Only the upper half of the tube and the top of the plate were treated with AquaFast. The bottom of the plate was not coated. The performance is self-evident.

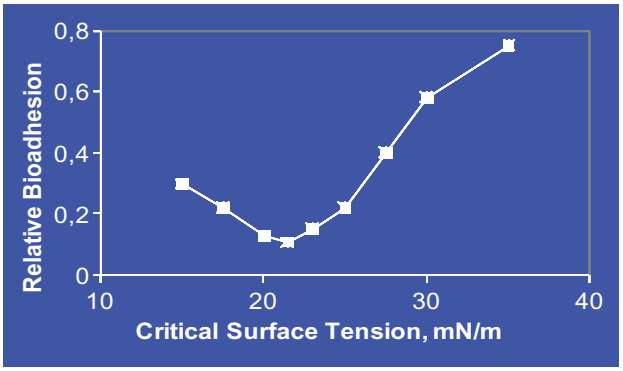

Figure 4. The ORMOSIL sol-gel paint Aquafast is in the zone of minimal bioadhesion.

(Baier and Meyer, 1992: 165) characterizes the first 4–5 Å of a surface and γ_C of surfaces measured by such analysis empirically and reproducibly characterizes the surface. Silica-based coating materials having a bulk cross-linked porous structure are ideally suited as protective coatings. The surface characteristics of hybrid xerogel AquaFast include a zone of minimal bioadhesion (Fig. 4) for surfaces with values of γ_C between 20 and 30 mN m^{-1} where weak boundary layers are formed, which allows biofouling to be removed by shear forces. Hybrid ORMOSIL xerogels are indeed in the zone of minimal bioadhesion with AquaFast having values of γC of 20 mN m^{-1}. Accordingly, this xerogel film gives significantly greater removal of biomass relative to the other xerogel films and glass controls, and also performs as a fouling-release surface for other species.

Outlook and conclusions

Underwater archaeology is of cultural, economic, and academic importance. Protection and promotion of underwater archaeology require a common strategy that allows access yet protects the site for future generations. The innovative STARS project is making the underwater cultural heritage accessible to a wider public through the World Wide Web. The well-developed website in Italian is currently being updated to include an English version and increase its accessibility. Given the large popular response to the pilot underwater trails in Pantelleria, more projects for archaeological underwater parks are being planned around Sicily by the Soprintendenza del Mare (http://www.regione.sicilia.it/beniculturali/sopmare) which has developed a number of ways to open up its underwater sites, either in the form of linear routes highlighting specific archaeological items, or controlled areas with a guide suitable for less-specific visits.

The use of ecofriendly antifouling coatings is highly recommended for protecting devices on such sites. In recent years a number of environmentally-benign and safe antifouling products have been developed thanks to advancements in nanochemistry (for example, the BioFlow SAFE sol-gel silica-epoxy paint commercialized by Safe Marine Nanotechnologies is a low-surface-energy paint which avoids adhesion of vegetation on ship's hulls without releasing poisonous chemicals into the water). Silica-based AquaFast is one of these products, and tests carried out over a 9-month period in the sea off Pantelleria show that little or no fouling occurs on (metal) surfaces treated with the product. The AquaFast coating exhibits a low-surface-energy surface that minimizes adhesion. Its application is easy and does not differ from traditional paints. Besides safeguarding the environment, such anti-fouling protection results in considerable economic savings, as mechanical cleaning is no longer required to remove the organisms which otherwise would clog the (expensive) device, interrupting the functioning of telecontrol. We are currently extending the use of the product to other sites in Sicily.

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New Boat Paintings from Angkor Wat?

While on fieldwork in Cambodia I found a set of paintings of boats in the outer gallery of the Angkor Wat temple. After consulting with Dr Christophe Pottier from the Ecole Française d'Extrème Orient and Dr Dan Penny from the Greater Angkor Project (GAP), we found out that the images had never been acknowledged by researchers. Angkor Wat is the most extensive religious monument in the world, so it is unsurprising that the paintings went unnoticed. The area where they are located is closed to visitors to preserve the integrity of the structure. The paintings are not of the same artistic quality as the carvings, and most probably date from a later period, so it would not be surprising that they were ignored by early scholars.

As seen in the image (Figs 1–4), the wall is covered with plaster and then painted with a red hue. The authenticity of the paintings could be debated, but they date at least from the 1980s, since there are bullet-holes in them (Fig. 3). However, there are some initial indications of a potentially older date. Buddhist monks redecorate their temples constantly (for example the Mogao Caves in China), and Angkor Wat has been in continuous use as a Buddhist sanctuary (Lyons *et al.* 1985: 63), so it would not be surprising if the paintings were done during a time of religious revival. In the bottom area of the image it is possible to see the carvings of *Apsaras* (celestial dancers) painted in the same colour as the paintings (Figs 2 and 4).

There is a three-masted vessel represented in the scene (Figs 1–4) and, according to Pottier, in some areas the plaster seems to run underneath the fragmentary remains of red-painted plaster which may date from the 16th–17th century, but more detailed research needs to be done before estimating a date. There are also orange-and-black sketches which could present a problem, since they appear to be quite modern. The images are very interesting, since some of them represent what could be interpreted as an awning structure (Fig. 4), a feature described by Zhou Daguan in the 13th century (2007: 78), but which we have been unable to find represented in the nautical scenes of Angkor. It is an interesting problem. I will be working on this subject for my PhD, and will hopefully be able to write a more extensive article regarding the dating and authenticity of the paintings in the near future.

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