# Cuaternario y Geomorfología

ISSN: 0214-1744



www.rediris.es/CuaternarioyGeomorfologia/

# Radiocarbon dating of marine shells from the Gulf of Cadiz: The marine radiocarbon reservoir effect, its variability during the Holocene and palaeoenvironmental inferences

Datación radiocarbónica de conchas marinas en el golfo de Cádiz: El efecto reservorio marino, su variabilidad durante el Holoceno e inferencias paleoambientales

Monge Soares, António M.

Grupo de Radiações, Elementos e Isótopos – Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal. amsoares@ctn.ist.utl.pt

#### Abstract

The ocean reservoir is deficient in radiocarbon compared with the atmosphere and, consequently, an offset in <sup>14</sup>C age exists between coeval samples containing marine carbon versus those containing terrestrial carbon. A record of past reservoir ages is preserved in the <sup>14</sup>C ages of contemporary marine and terrestrial material. The quantification of the marine radiocarbon reservoir effect ( $\Delta R$ ) is of crucial importance to the correct calibration of the <sup>14</sup>C ages of marine samples. For the southern Atlantic Iberian coast, during the last 3000 yr,  $\Delta R$  takes the following values +69±17 <sup>14</sup>C yr (Barlavento coast), -26±14 <sup>14</sup>C yr (Sotavento coast), and -108±31 <sup>14</sup>C yr (Andalusian coast), which are in accordance with the oceanographic conditions present in each area. Results also suggest that during the 5th millennium cal BP very different oceanographic conditions (high positive  $\Delta R$  values) prevail in the Barlavento and in the Atlantic Andalusian coastal areas and, consequently, in all the northern Gulf of Cadiz region, perhaps due to the extension of the Azores Front eastward along the Azores Current penetrating into the Gulf of Cadiz.

Keywords: Radiocarbon dating, reservoir effect, Holocene, Gulf of Cadiz.

#### Resumen

El reservorio de radiocarbono oceánico es deficitario en comparación con el atmosférico y, como consecuencia, existe un desfase de <sup>14</sup>C entre muestras equivalentes con carbono de procedencia marina y continental. Las edades radiocarbónicas de muestras contemporáneas, procedentes de ambos medios, conservan un registro de los reservorios pasados y de su evolución temporal. La cuantificación del efecto reservorio radio-

Derechos de reproducción bajo licencia Creative Commons 3.0. Se permite su inclusión en repositorios sin ánimo de lucro.



carbónico marino ( $\Delta$ R) es muy importante en la correcta calibración de las edades de <sup>14</sup>C procedentes de muestras marinas. Durante los últimos 3.000 años, los valores de  $\Delta$ R en la costa atlántica ibérica meridional han seguido las fluctuaciones de las condiciones oceanográficas de cada sector, así, en la costa de Barlovento (Portugal) el valor medio es de +69±17 años <sup>14</sup>C, -26±14 años <sup>14</sup>C en la costa de Sotavento (Portugal) y -108±31 años <sup>14</sup>C en la costa de Andalucía occidental (España). Los resultados también sugieren que durante el V milenio cal BP existieron unas condiciones oceanográficas muy diferentes (valores muy altos de  $\Delta$ R) en las costas de Barlovento y Andalucía, y por lo tanto en todo el sector ibérico del golfo de Cádiz, debido quizás a la penetración hacia el este del Frente de las Azores, siguiendo la entrada de la corriente de las Azores en el golfo de Cádiz.

Palabras clave: Datación radiocarbono, efecto reservorio, Holoceno, Golfo de Cádiz.

#### 1. Introduction

Radiocarbon (<sup>14</sup>C) dates on marine samples (usually marine shells) have not been used as extensively as charcoal or bone dates for the setting up of absolute chronologies because interpreting these dates is complicated by the spatial and temporal variability of the oceanographic conditions which is reflected in the so-called marine radiocarbon reservoir effect. Nevertheless marine shellfish were used widely by human populations at least during the Holocene and their shells are abundant and usually well preserved in archaeological deposits located near shorelines. Their radiocarbon content reflects the content of this element in the marine environment where the shells were formed. Consequently this <sup>14</sup>C content value not only allows to infer changes occurring over time in the environment where the shells grew or in related geophysical reservoirs, but also by their dating to determine the chronology of the sedimentary sequence from where they have been collected. For this reason, prior research concerning the oceanographic conditions and the marine radiocarbon reservoir effect ( $\Delta R$ ) of a particular coastal area is needed in order to set up reliable chronologies for that region. The quantification of  $\Delta R$  is of crucial importance to the correct calibration of the <sup>14</sup>C ages of marine samples and thereafter to build up reliable and accurate chronologies.

In the present study, the results concerning the determination of the marine radiocarbon

reservoir effect for the coastal waters of the Gulf of Cadiz are presented and discussed. From now on archaeologists and geologists working in this region will have the possibility to set up more accurate and reliable radiocarbon chronologies for Holocene events, for prehistoric sites and cultural phases that took place at the territories bordering the Gulf of Cadiz just to the north. Besides the importance of these issues, the quantification of the marine radiocarbon reservoir effect also allows a better knowledge of the palaeoceanography and palaeoclimatology of the Southern Atlantic Iberia.

# 2. The marine radiocarbon reservoir effect (ΔR)

As is well known, the ocean reservoir is deficient in radiocarbon compared with the atmosphere. The residence time of carbon in the deep ocean is about 1000 yr (Sigman and Boyle, 2000). Thus a fraction of the <sup>14</sup>C atoms have time to decay (the <sup>14</sup>C half-life is 5730 yr) while the deep water is out of contact with the atmosphere. The deep ocean is therefore depleted in <sup>14</sup>C relative to the atmosphere, and consequently the surface seawater (mixed layer) also has a <sup>14</sup>C specific activity lower than that of the atmosphere but greater than that of the deep ocean. Therefore a <sup>14</sup>C reservoir age exists for the ocean, i.e. an offset in <sup>14</sup>C age exists between coeval samples containing marine carbon versus those containing terrestrial carbon. Following Stuiver et al. (1986) the marine radiocarbon reservoir age, R(t), can be defined as the difference between conventional <sup>14</sup>C dates from a pair of coeval samples that lived in different carbon reservoirs (marine and terrestrial biosphere). R(t) is time-dependent due to variations of <sup>14</sup>C content in the atmosphere and differences between transfer rates of <sup>14</sup>C between the atmosphere and the ocean reservoir through time. Reservoir age is also variable from region to region of the ocean (Stuiver et al., 1986; Stuiver and Braziunas, 1993; Reimer et al., 2002; Reimer and Reimer, 2006) since the oceanographic conditions present in each region are different due to variations in reservoir parameters such as water mass mixture, wind regime, bathymetry, and upwelling of deep water.

Considering these issues Stuiver et al. (1986) modelled the response of the world ocean to atmospheric <sup>14</sup>C variations. From this modelling two calibration curves for marine samples have been derived: one related to the deep ocean and the other to the sea surface water (mixed layer). Besides, in order to take into account the difference in <sup>14</sup>C content between the surface water of a specific region and the average surface water, a parameter, denoted as  $\Delta R$  (regional marine <sup>14</sup>C reservoir effect), is defined as the difference between the reservoir age of the mixed layer of the regional ocean and the reservoir age of the mixed layer of the average world ocean in AD 1950 (Stuiver et al., 1986).  $\Delta R$  values are often determined for a particular geographical region by <sup>14</sup>C dating of pairs of samples of the same age but of different origin (terrestrial and marine) and converting the terrestrial biosphere sample <sup>14</sup>C age into a marine model age; this marine model age is then deducted from the <sup>14</sup>C age of the associated marine sample to yield  $\Delta R$  (Stuiver and Braziunas, 1993). Although reservoir ages are time-dependent,  $\Delta R$  is not unless some change of oceanographic conditions restricted to the considered regional ocean has occurred. This happens, for instance, in regions affected by the upwelling of deep water. Since rates of regional upwelling can vary in the course of time, and the intensity of the <sup>14</sup>C depletion in the mixed layer depends upon the strength of wind-driven coastal upwelling, it is likely that values of  $\Delta R$  can also vary in the course of time (Kennett *et al.*, 1997; Ingram, 1998; Ascough *et al.*, 2005; Soares, 2005; Soares and Dias, 2006, 2007). Positive high  $\Delta R$  values can be correlated with a strong upwelling, while low or negative  $\Delta R$  values correspond with a weak, or even non-existent, upwelling. As a measure of the regional enhancement or depletion of <sup>14</sup>C,  $\Delta R$  can also be used as an upwelling proxy, which provides the most direct signal of upwelling activity (Diffenbaugh *et al.*, 2003).

It must be noted that R(t) and  $\Delta R$ , although connected with the marine radiocarbon reservoir effect, are different entities and users of radiocarbon dates of marine samples should not confuse these entities that have different definitions and meanings (Soares, 2010; Rodríguez-Vidal et al., 2010). R(t) is always positive, taking into consideration its definition mentioned above, while  $\Delta R$  can be either positive or negative (Stuiver and Braziunas, 1993; Stuiver et al., 2009). ΔR is the parameter that has to be known when a marine radiocarbon date is calibrated, i.e. converted in calendar years. Marine13 is the last calibration curve published (Reimer et al., 2013) for the mixed layer, the most widely used and its use internationally recommended.

Along the western coasts of Europe, active wind-driven coastal upwelling is, at present, practically restricted to the Atlantic coast of the Iberian Peninsula, particularly from Cape Finisterra to Cape São Vicente. A research concerning the reservoir effect in the coastal waters off the western Atlantic Iberian Peninsula enabled a clarification concerning the variability of the wind-driven coastal upwelling off Atlantic Iberia along the Holocene (Soares, 2005; Soares and Dias, 2006, 2007).  $\Delta R$  values, although usually strongly positives, e.g. 250±25 <sup>14</sup>C yr for the modern value or a value of 95±15 <sup>14</sup>C yr for the time interval between 3000 to ≈600 BP, suggest a significant fluctuation with time in the strength of the coastal upwelling in the western Portuguese coast between Aveiro and Faro, and also off north-western Galicia. On the other hand, a recent study concerning the <sup>14</sup>C content determination of marine mollusc shells collected off the European Atlantic margin between 45° N and 60° N showed that  $\Delta R$ takes the value of -7±50 <sup>14</sup>C yr (Tisnérat-Laborde et al., 2010) which is in accordance with the prevailing oceanographic conditions of that region influenced by the North Atlantic Current and where the coastal upwelling is not present. Another example could be the research carried out concerning the Canary Archipelago. Coastal Fuerteventura has a positive weighted mean  $\Delta R$  value of +185±30 <sup>14</sup>C yr, while for Tenerife the weighted mean  $\Delta R$  value is 0±35 <sup>14</sup>C yr (Martins *et al.*, 2012). These values are in accordance with the hydrodynamic system present off the Canary Islands characterized by a coastal upwelling regime that affects the eastern islands (Fuerteventura and Lanzarote) but not the other islands of the archipelago, namely Tenerife. Because of this oceanographic pattern, the extrapolation of these results can be done to the remaining islands of the archipelago, i.e. the first value must be used for the eastern islands, while for the central and western islands the acceptable  $\Delta R$  value is 0±35 <sup>14</sup>C yr These examples are intended to show the importance of knowledge of the oceanographic conditions and also of the  $\Delta R$  (marine radiocarbon reservoir effect) value or values prevailing in a particular regional ocean in order to set up reliable and accurate chronologies for the events that have occurred in the land territories bordering that sea.

# 3. The Gulf of Cadiz

# 3.1. Oceanographic conditions

The Gulf of Cadiz receives and mixes outflowing Mediterranean water and is influenced by Portuguese and Moroccan coastal currents, and by an extension of the Azores Current. South of the Azores Islands, the Azores Current coincides with the Azores Front, which marks the north-eastern boundary of the North Atlantic subtropical gyre. The Azores Front corresponds to a zone of strong hydrographical transition, not only in terms of temperature but also in the structure of the water column, and is characterized by locally intense upwelling (Rogerson *et al.*, 2004). The Azores Front does not penetrate into the Gulf of Cadiz at present, even though the Front resides in the Atlantic Ocean at the same latitude as the Gulf of Cadiz. These various influences result in a complex circulation pattern in the Gulf of Cadiz.

The Portuguese southern coast (Algarve) is oriented along 37º N, between 7º 20' W and 9º W (Fig. 1). The regime of winds is strongly correlated with the latitudinal migration of the subtropical front and with the dynamics of the Azores anticyclone cells. Hence, the atmospheric circulation associated with the Azores high corresponds to westerly winds in winter and to northerly and north-westerly winds with considerably more strength in summer. These northerly summer winds induce Ekman transport offshore along the western Iberian coast, i.e. they are clearly upwelling favourable in that coastal region, while westerly winds can induce this phenomenon in the southern coast.

The western part of the Portuguese southern coast, i.e. the western part of the northern coast of the Gulf of Cadiz, the so-called Barlavento (windward) region, located between Cape San Vicente and Cape Santa Maria (Fig. 1), is influenced by the dynamic effect of Cape San Vicente that allows upwelled water present along the western Portuguese coast to move south-eastward and eastward, creating a quasi-permanent upwelling area around the cape (Fiúza, 1982, 1983; Fiúza *et al.*, 1982; Ferreira, 1984).

The central part of the northern coast of the Gulf of Cadiz, the so-called Sotavento (leeward) region, located between Cape Santa Maria and the mouth of the Guadiana River, can also be influenced by the upwelling phenomenon, although in this region it presents



Figure. 1: Location of coastal areas and archaeological sites analysed herein. Figura. 1: Situación de los sectores costeros y lugares argueológicos analizados.

a week activity. When the prevailing winds in the Gulf of Cadiz are from the west, a minor upwelling area occurs offshore to the east of Cape Santa Maria (Vargas *et al.*, 2003).

Finally, in the eastern part of the southern Iberian Atlantic coast (the Andalusian coast), due to its configuration describing an arc between the mouth of the Guadiana River and the Strait of Gibraltar the wind-driven coastal upwelling is non-existent, contrarily to the situation occurring off other coasts of the Atlantic Iberia, from Cape Ortegal to Cape São Vicente and even at the southern coast of Portugal as mentioned above.

Taking into account these oceanographic conditions occurring off the southern Atlantic Iberian coast it seems that the Sotavento region will be a transition zone between a region, the Barlavento, where upwelled waters are important due to the influence of the western coastal upwelling system and an area, the western Andalusian coast of the Gulf of Cadiz, where the upwelling regime is absent. Since the  $\Delta R$  is an upwelling proxy, the values of this parameter for these three regions should be in accordance with the oceanographic conditions, i.e. it is expected a positive value for Barlavento, most likely a negative value for the Andalusian coast and between these values the value for the Sotavento.

# 3.2. The marine <sup>14</sup>C reservoir effect

Pairs of closely associated archaeological samples (marine shells/charred wood or bones) from each depositional context were collected from archaeological sites present in Barlavento, Sotavento and Andalusian regions (see Fig. 1). Sampling and analytical procedures are described in detail elsewhere (Martins and Soares, 2013; Soares, 2005; Soares and Dias, 2006, 2007). Radiocarbon ages were calculated in accordance with the definitions recommended by Stuiver and Polach (1977).  $\Delta R$  values were determined by converting the terrestrial biosphere sample <sup>14</sup>C age into a marine model age. This marine model age was subtracted from the <sup>14</sup>C age of the associated marine shell sample to yield  $\Delta R$  using a methodology based on Ascough et al. (2005, 2007, 2009) and Russell et al. (2011). The reservoir age R(t), i.e. the difference between conventional <sup>14</sup>C dates from a pair of coeval samples that lived in different carbon reservoirs, was also determined.  $\Delta R$  and R(t) values are listed in Table 1.

Fifteen  $\Delta R$  values were determined for the Barlavento coast but three (+527 ± 54 <sup>14</sup>C yr, +553 ± 86 <sup>14</sup>C yr, and +380 ± 75 <sup>14</sup>C yr) were rejected in the calculation of the  $\Delta R$  weighted mean value taking into account the  $\chi^2$  results (127.25; ( $\chi^2_{;0.05}$ =23.68)). With the remaining twelve values a  $\Delta R$  weighted mean value of +69 ± 17 <sup>14</sup>C yr was determined for this coastal region.

Regarding the Sotavento region, thirteen  $\Delta R$  values were obtained but one (+190 ± 51 <sup>14</sup>C yr) was rejected, being the remaining twelve values statically indistinguishable [17.75; ( $\chi^2_{.0.05}$ =19.68)]. A  $\Delta R$  weighted mean value of -26 ± 14 <sup>14</sup>C yr was thereby obtained for the Sotavento coastal region.



Figure 2:  $\Delta R$  (±1 $\sigma$ ) values for the 3 coastal regions plotted versus terrestrial <sup>14</sup>C ages (±1 $\sigma$ ). Figure 2: Valores de  $\Delta R$  (±1 $\sigma$ ) de los tres sectores costeros, comparados con edades de <sup>14</sup>C (±1 $\sigma$ ) terrestre.

For the Andalusian coast two  $\Delta R$  weighted mean values were obtained. Two sets of  $\Delta R$ values were considered in the calculation of the weighted mean value, namely the three positive values (+200 ± 66 <sup>14</sup>C yr, +98 ± 106 <sup>14</sup>C yr, and +327 ± 233 <sup>14</sup>C yr) resulting in a  $\Delta R$ weighted mean value of +180 ± 66 <sup>14</sup>C yr, and the remaining six negative values with a  $\Delta R$ weighted mean value of -108 ± 31<sup>14</sup>C yr.

If the  $\Delta R$  data present in Table 1 are plotted against time (Fig. 2) the variability of the  $\Delta R$ can be observed and compared among the three coastal regions. The high positive  $\Delta R$ values can be correlated with the presence of the upwelling phenomenon, while low or negative  $\Delta R$  values correspond to a weak, or even non-existent, upwelling. The Barlavento coast has the higher values of  $\Delta R$ , the Andalusian coast the more negative ones and the Sotavento coast, a transition zone as mentioned before, has values between these two as expected. The  $\Delta R$  values that were determined for the three regions are, consequently, in accordance with the existent oceanographic conditions. The highly negative values obtained for the Andalusian coast are consistent with a non-existent coastal upwelling, also suggesting some stratification of the water column.

However, it must be noted that before 3 ka BP positive  $\Delta R$  values were determined for the Andalusian coast and higher positive values for the Barlavento coast strongly suggesting a major change in the oceanographic conditions prevailing in the entire region of the southern Iberian Atlantic coast (see rejected values in the calculation of the  $\Delta R$  weighted mean for the Barlavento coastal region). A similar situation has already been verified in this same region in two periods between the Last Glacial Maximum and the Holocene, which can be explained by the extension of the Azores Front eastward along the Azores Current into the Gulf of Cadiz (Rogerson et al., 2004). Taking into account that a strong upwelling is always associated with the Azores Front the positive  $\Delta R$  values that were determined for the time period mentioned above can be easily explained.

Besides this, at 866 ± 50 BP, a peak ( $\Delta R$ = +190 ± 51<sup>14</sup>C yr) in the  $\Delta R$  dataset from the Sotavento coast was obtained, which match another peak ( $\Delta R$ = +587 ± 125 <sup>14</sup>C yr) obtained at 872 ± 90 BP in the western Portuguese coast (Soares and Dias, 2006) and another one ( $\Delta R$ = +270 ± 40 <sup>14</sup>C yr) obtained at 860 ± 90 BP in the western Galician coast (Soares and Dias, 2007). These synchronous peaks (see Fig. 3) can be related with the cold event found at 0.8 ka cal BP by deMenocal *et al.* (2000) which in turn can be related with the climatic reorganization associated with the end of the Medieval Warm Period and the beginning of the Little Ice Age.

Finally, in the field of practical application of the  $\Delta R$  values determined for the Andalusian Atlantic coast, it should be noted that the existence of such different two values for  $\Delta R$  can introduce some uncertainty when performing the calibration of conventional radiocarbon dates of marine shells from the 5th millennium BP. Table 1 shows in the 2nd column the weighted age of terrestrial and marine samples of the dated pairs and it can be seen that the first four radiocarbon dates (Papa Uvas E15, Papa Uvas FIV, La Viña Silo 16, Papa Uvas F12) are statistically indistinguishable at 95% level [1.46; ( $\chi^2_{:0.05}$ =7.81)]. However, with these pairs two different  $\Delta R$  weighted mean values were calculated. Also the respective R(t) values of those four dates can be assembled in two groups (see Table 1, last column): 240±130 <sup>14</sup>C yr, 285±63 <sup>14</sup>C yr; 521±63 <sup>14</sup>C yr, 439±115 <sup>14</sup>C yr. Looking at R(t) values in Table 1 it can be verified that R(t) will take an approximate value of 250 <sup>14</sup>C yr for the mentioned negative  $\Delta R$  values or *ca.* 480 <sup>14</sup>C yr for the positive ones. Taking into account this desideratum a shell sample collected in the Andalusian Atlantic coast with a true age of 4350 BP will have an apparent age of ca. 4800 BP, while another shell sample with a true age of 4550 BP will have the same apparent age. So, *a priori*, we do not know which  $\Delta R$  we must



Figure 3: The synchronous peaks around 870 BP. Figure 3: Valores máximos alrededor de hace unos 870 años BP. Table 1.  $\Delta R$  and R(t) values for the three areas of the

northern Gulf of Cadiz region (Barlavento, Sotavento and Andalusia).

use for the calibration of those dates. If those dates are from a sequence and we are using a Bayesian model it will perhaps be possible to choose one of the values taking into account the value obtained for the model agreement. For other cases using marine shell dates from the 5th millennium BP it will be hard to choose which of the two  $\Delta R$  values should be used.

#### 4. Conclusions

A record of past reservoir ages is preserved in the <sup>14</sup>C ages of contemporary marine and terrestrial material, which can provide valuable information concerning the palaeointensity of coastal upwelling or of other palaeoenvironmental processes in marine regions. Table 1:  $\Delta R$  and R(t) values for the three areas of the northern Gulf of Cadiz region (Barlavento, Sotavento and Andalusia).

Tabla 1: Valores de  $\Delta R$  y R(t) para los tres sectores costeros del golfo de Cádiz septentrional (Barlovento, Sotavento y Andalucía).

Archaeological Context		<sup>14</sup> C age (BP) <sup>1</sup>	cal BC/AD (2σ)	cal BP (2σ)	$\Delta \mathbf{R}$ ( <sup>14</sup> C yr)	R(t) ( <sup>14</sup> C yr)				
			Barlovento <sup>2,3</sup>							
Alcalar	M7	5636 ± 97 (6520±40)	4710 – 4330 cal BC	6659 - 6279	+527 ± 54ª	892±58				
Pedra Escor.	-	3985 ± 55 (4870±40)	2834 – 2300 cal BC	4783 – 4249	+553 ± 86ª	908±49				
Alcalar	[781]	3957 ± 45 (4490±51)	2576 – 2306 cal BC	4525 – 4255	+158 ± 64	533±68				
Rocha Branca	QD3	2566 ± 42 (3010±45)	813 – 544 cal BC	2762 – 2493	+79 ± 73	443±61				
Rocha Branca	QE3	2391 ± 44 (2880±50)	750 – 389 cal BC	2699 - 2338	+158 ± 58	493±66				
P.J. Faro	EA	2234 ± 40 (2640±50)	390 – 203 cal BC	2339 – 2152	+40 ± 74	410±64				
V.V. Alvor	-	2105 ± 65 (2480±70)	359 cal BC – 24 cal AD	2308 - 1927	+36 ± 110	382±95				
Loulé Velho	Abside	2028 ± 72 (2480±50)	345 cal BC – 128 cal AD	2294 - 1823	+113 ± 87	450±89				
Loulé Velho	2	1754 ± 44 (2130±45)	138 – 392 cal AD	1812 – 1558	+32 ± 62	372±64				
P.C. Silves	Q30	1277 ± 38 (1620±40)	659 – 861 cal AD	1292 - 1090	-51 ± 64	345±54				
P.C. Silves	Q4	1139 ± 45 (1880±70)	776 – 992 cal AD	1174 – 959	+380 ± 75°	743±83				
R. Arrochela	Silo 4	1060 ± 41 (1490±30)	891 – 1029 cal AD	1060 - 921	+67 ± 35	435±40				
Lagos	RJ306	564 ± 36 (1056±33)	1302 – 1430 cal AD	648 – 520	+59 ± 55	492±49				
Lagos	RJ37	539 ± 34 (1040±39)	1312 – 1440 cal AD	638 – 511	+77 ± 47	501±52				
Lagos	RJ86	423 ± 35 (984±40)	1419 – 1620 cal AD	531 - 330	+106 ± 49	561±53				
Weighted Mean Calculation for ΔR		$\chi^2_{:0.05=}$ T (1st test)	127.25; (χ <sup>2</sup> <sub>:0.05</sub> =23.68)	<sup>a</sup> – rejected values						
	$\chi^2_{-0.05}$ T (2nd test) 9.32; ( $\chi^2_{-0.05}$ =19.68)									
	Weig	hted Mean: ΔR=+ <b>69 ± 17</b> <sup>14</sup> C γ	<b>yr</b> Modern value³: <b>ΔR=+353</b> ±	32 <sup>14</sup> C yr						
			Sotavento <sup>3</sup>							
Castro Marim	UE 340	2458 ± 82 (2755±45)	782 – 402 cal BC	2731 – 2351	-51 ± 113	297±94				
Castro Marim	UE 345	2447 ± 83 (2752±37)	780 – 398 cal BC	2729 – 2347	-37 ± 97	305±91				
Castro Marim	UE 89	2438 ± 34 (2671±32)	752 – 406 cal BC	2701 – 2355	-120 ± 41	224±34				
Castro Marim	UE 215	2431 ± 55 (2740±47)	757 – 401 cal BC	2706 – 2350	-7 ± 65	309±72				
Castro Marim	UE 124	2427 ± 68 (2660±34)	764 – 397 cal BC	2713 – 2346	-146 ± 81	228±60				
Castro Marim	UE 299	2419 ± 41 (2771±60)	752 – 399 cal BC	2701 – 2348	-11 ± 100	352±73				
Tavira	RAF	1662 ± 58 (1984±48)	252 – 536 cal AD	1669 - 1415	-44 ± 76	322±75				
Cacela	UE 405	866 ± 50 (1447±34)	1040 – 1260 cal AD	910 - 690	+190 ± 51 <sup>b</sup>	575±50				
Cacela	UE 410	860 ± 36 (1257±20)	1046 – 1260 cal AD	905 - 690	+26 ± 26	401±28				
Tavira	CSM	839 ± 32 (1133±40)	1057 – 1265 cal AD	893 - 685	-80 ± 42	291±43				
Tavira	Sap.5	708 ± 36 (1178±37)	1227 – 1389 cal AD	723 – 562	+55 ± 41	470±52				
Tavira	Sap.6	649 ± 29 (998±42)	1281 – 1395 cal AD	670 – 556	-59 ± 52	349±41				
Tavira	CNSP	271 ± 27 (647±25)	1520 – 1797 cal AD	430 - 153	-37 ± 32	381±26				
Weighted Mean Calculation for $\Delta R$		$\chi^2_{:0.05=}$ T (1st test)	34.59; (χ <sup>2</sup> <sub>:0.05</sub> =21.	03)	<sup>b</sup> – rejected value					
	$\chi^2_{:0.05}$ = 7 (2nd test) 17.75; ( $\chi^2_{:0.05}$ =19.68)									
	Weighted Mean: $\Delta R$ =-26 ± 14 <sup>14</sup> C yr Modern value <sup>3</sup> : $\Delta R$ =+17±52 <sup>14</sup> C yr									

Andalusian coast <sup>2,3</sup>										
Papa Uvas	E15	4574 ± 108 (4820±70)	3632 – 2942 cal BC	5581 - 4891	-117 ± 114°	242±128				
Papa Uvas	FIV	4475 ± 49 (4760±55)	3357 – 2945 cal BC	5306 - 4894	-103 ± 80 °	285±63				
La Viña	Silo 16	4428 ± 83 (4960±40)	3345 – 2911 cal BC	5294 - 4860	+200 ± 66 <sup>d</sup>	521±63				
Papa Uvas	F12	4421 ± 94 (4850±70)	3355 – 2898 cal BC	5304 - 4847	$+98 \pm 106^{d}$	425±120				
Papa Uvas	B10	4054 ± 195 (4740±50)	3308 – 2027 cal BC	5257 – 3976	+327 ± 233 <sup>d</sup>	681±202				
Niebla	UE69	2067 ± 65 (2240±80)	351 cal BC – 71 cal AD	2300 - 1880	-163 ± 105 °	176±103				
El Eucaliptal	UE 4	1751 ± 84 (1960±30)	73 – 530 cal AD	1877 – 1421	-142 ± 73 °	203±69				
Niebla	UE16	904 ± 40 (1180±70)	1033 – 1213 cal AD	917 - 737	-82 ± 77 °	272±83				
Niebla	SA	218 ± 43 (550±40)	1524 – 1955 cal AD	427 – 0	-88 ± 54 °	337±57				
Weighted Mean Calculation for $\Delta R$ ( <sup>c</sup> negative $\Delta R$ values)			$\chi^{2}_{:0.05=}$ <i>T</i> (test 1)	0,75; (χ² <sub>:0.05</sub> =11.07)						
		Weighted Mean:	∆R= <b>-108 ± 31¹⁴C yr</b>							
Weighted Mean Calculation for $\Delta R$ ( <sup>d</sup> positive $\Delta R$ values)			$\chi^2_{:0.05=}$ <i>T</i> (test 1)	1,09; (χ² <sub>:0.05</sub> =5.99)						
Weighted Mean: ΔR=+ <b>180 ± 66</b> <sup>14</sup> C γr										

<sup>1</sup> Values in brackets refer to marine samples. <sup>2</sup>Soares and Martins (2009, 2010).

<sup>3</sup>Martins (2014); Martins and Soares (2013).

 $\Delta R$  weighted mean values determined for the last 3000 years –  $\Delta R$  = + 69 ± 17 <sup>14</sup>C yr (Barlavento coast);  $\Delta R$  = -26 ± 14 <sup>14</sup>C yr (Sotavento coast);  $\Delta R$  = -108 ± 31 <sup>14</sup>C yr (Andalusian coast) – are in accordance with the oceanographic conditions present in each area.

On the other hand, the obtained data suggests that very different oceanographic conditions (high positive  $\Delta R$  values) prevail in Barlavento and Andalusian coastal areas and, consequently, in all the northern Gulf of Cadiz region during the 5th millennium cal BP, perhaps due to the extension of the Azores Front eastward along the Azores Current penetrating into the Gulf of Cadiz. Finally, a peak in the  $\Delta R$  data set for the Sotavento coast was identified at 866 ± 50 BP, which can be related to the cold event that took place at 0.8 ka cal BP.

Using the obtained  $\Delta R$  values with the calibration curve Marine13 is currently the best approach to calibrate marine shell radiocarbon dates in order to set up reliable and accurate chronologies.

### References

- Ascough, P.L.; Cook, G.T.; Dugmore, A.J. (2005). Methodological approaches to determining the marine radiocarbon reservoir effect. *Progress in Physical Geography*, 29(4), 532-547.
- Ascough, P.L.; Cook, G.T.; Dugmore, A.J.; Scott, E.M. (2007). The North Atlantic Marine Reservoir Effect in the Early Holocene: Implications for Defining and Understanding MRE Values. *Nuclear Instruments and Methods in Physics* B, 259(1), 438-447.
- Ascough, P.L.; Cook, G.T.; Dugmore, A.J. (2009). North Atlantic Marine 14C Reservoir Effects: implications for late-Holocene chronological studies. *Quaternary Geochronology*, 4(3), 171-180.
- de Menocal, P.B.; Ortiz, J.; Guilderson, T.; Sarnthein, M. (2000). Coherent high- and low-latitude climate variability during the Holocene warm period. *Science*, 288(5474), 2198–2202.
- Diffenbaugh, N.S.; Sloan, L.C.; Snyder, M.A. (2003). Orbital suppression of wind-driven upwelling in the California Current at 6 ka. *Paleoceanography*, 18 (2), 1051, doi:10.1029/2002PA000865.
- Fiúza, A.F.G. (1982). The Portuguese Coastal Upwelling System. In: *Actual Problems of Oceanography in Portugal*. Junta Nacional de

Investigação Científica e Tecnológica, Lisbon, 45-71.

- Fiúza, A.F.G. (1983). Upwelling Patterns off Portugal. In: Coastal Upwelling. Its Sediment Record (E. Suess; J. Thiede, eds.). Plenum, New York, 85-98.
- Fiúza, A.F.G.; Macedo, M.E.; Guerreiro, M.R. (1982). Climatological space and time variation of the Portuguese coastal upwelling. *Oceanologica Acta*, 5, 31-40.
- Ferreira, D.B. (1984). *Le Systeme Climatique de l'Upwelling Ouest Iberique*. Report #19 of the Linha de Acção de Geografia Física. Centro de Estudos Geográficos. INIC, Lisbon.
- Ingram, B.L. (1998). Differences in radiocarbon age between shell and charcoal from a Holocene Shellmound in Northern California. *Quaternary Research*, 49 (1), 102–110.
- Kennett, D.J.; Ingram, B.L.; Erlandson, J.M.; Walker, P. (1997). Evidence for temporal fluctuations in marine radiocarbon reservoir ages in the Santa Barbara Channel, southern California. *Journal of Archaeological Science*, 24 (11), 1051-1059.
- Martins, J.M.M. (2014). A Plataforma Continental Algarvia como arquivo de Paleoambientes e Paleoclimas Holocénicos. O papel do <sup>14</sup>C no seu estudo. PhD thesis, Faculdade de Ciências e Tecnologia, Universidade do Algarve, Faro, Portugal.
- Martins, J.M.M.; Mederos Martín, A.; Portela, P.J.C.; Soares, A.M.M. (2012). Improving the <sup>14</sup>C dating of marine shells from the Canary Islands for constructing more reliable and accurate chronologies. *Radiocarbon*, 54 (3-4), 943-952.
- Martins, J.M.M.; Soares, A.M.M. (2013). Marine Radiocarbon Reservoir Effect in Southern Atlantic Iberian Coast. *Radiocarbon*, 55 (2-3), 1123-1134.
- Reimer, R.W.; Reimer, P.J. (2006). Marine reservoir corrections and the calibration curve. *PAGES News*, 14(3), 12-13.
- Reimer, P.J.; McCormac, G.; Moore, J.; McCormick, F.; Murray, E.V. (2002). Marine radiocarbon reservoir corrections for the mid- to late Holocene in the eastern subpolar North Atlantic. *The Holocene*, 12 (2), 129-135.
- Reimer, P.J.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Bronk Ramsey, C.; Buck, C.E.; Cheng, H.; Edwards, R.L.; Friedrich, M.; Grootes, P.M.; Guilderson, T.P.; Haflidason, H.; Hajdas, I.; Hatté, C.; Heaton, T.J.; Hoffmann, D.L.; Hogg, A.G.; Hughen, K.A.; Kaiser, K.F.; Kromer, B.; Manning, S.W.; Niu, M.; Reimer, R.W.; Richards, D.A.; Scott, E.M.; Southon, J.R.; Staff, R.A.; Turney, C.S.M.; van der Plicht,

J. (2013). IntCal13 and Marine13 Radiocarbon Age Calibration Curves, 0-50,000 Years cal BP. *Radiocarbon*, 55 (4), 1869–1887.

- Rodríguez-Vidal, J.; Soares, A.M.M.; Ruiz, F.; Cáceres, L.M. (2010). Comment on "Formation of chenier plain of the Doñana marshland (SW Spain): Observations and geomorphic model, by A. Rodriguez-Ramírez and C.M. Yáñez-Camacho, in Marine Geology (2008), 254, 187-196". Marine Geology, 275 (1-4), 292-295.
- Rogerson, M.; Rohling, E.J.; Weaver, P.P.E.; Murray, J.W. (2004). The Azores Front since the Last Glacial Maximum. *Earth and Planetary Science Letters*, 222, 779-789.
- Russell, N.; Cook, G.T.; Ascough, P.L.; Scott, E.M.; Dugmore, A.J. (2011). Examining the inherent variability in  $\Delta R$ : New methods of presenting  $\Delta R$  values and implications for MRE studies. *Radiocarbon*, 53 (2), 277-288.
- Sigman, D.M.; Boyle, E.A. (2000). Glacial/interglacial variations in atmosphere carbon dioxide. *Nature*, 407, 859-869.
- Soares, A.M.M. (2005). Variabilidade do "Upwelling" Costeiro durante o Holocénico nas Margens Atlânticas Ocidental e Meridional da Península Ibérica. PhD thesis, Faculdade de Ciências do Mar e do Ambiente, Universidade do Algarve, Faro, Portugal.
- Soares, A.M.M. (2010). Comment on "Formation of chenier plain of the Doñana marshland (SW Spain): Observations and geomorphic model, by A. Rodriguez-Ramírez and C.M. Yáñez-Camacho, in Marine Geology 254 (2008) 187-196". Marine Geology, 275 (1-4), 287-289.
- Soares, A.M.M.; Dias, J.M.A. (2006). Coastal upwelling and radiocarbon – evidence for temporal fluctuations in ocean reservoir effect off Portugal during the Holocene. *Radiocarbon*, 48 (1), 45-60.
- Soares, A.M.M.; Dias, J.M.A. (2007). Reservoir effect of coastal waters off western and northwestern Galicia. *Radiocarbon*, 49 (2), 925-936.
- Soares, A.M.M.; Martins, J.M.M. (2009). Radiocarbon dating of marine shell samples. The marine radiocarbon reservoir effect of coastal waters off Atlantic Iberia during Late Neolithic and Chalcolithic periods. *Journal of Archaeological Science*, 36 (12), 2875-2881.
- Soares, A.M.M.; Martins, J.M.M. (2010). Radiocarbon dating of marine samples from Gulf of Cadiz: the reservoir effect. *Quaternary International*, 221 (1-2), 9-12.
- Stuiver, M.; Braziunas, T.F. (1993). Modeling Atmospheric <sup>14</sup>C Influences and <sup>14</sup>C Ages of

Marine Samples to 10,000 BC. *Radiocarbon*, 35(1), 137-189.

- Stuiver, M.; Polach, H.A. (1977). Discussion. Reporting of <sup>14</sup>C Data. *Radiocarbon*, 19 (3), 355-363.
- Stuiver, M.; Pearson, G.W.; Braziunas, T. (1986). Radiocarbon age calibration of marine samples back to 9000 cal yr BP. *Radiocarbon*, 28 (2B), 80-1021.
- Stuiver, M.; Reimer, P.J.; Reimer, R. (2009). Marine Reservoir Correction Database. http://calib. qub.ac.uk/calib/2009.
- Tisnérat-Laborde, N.; Paterne, M. ; Métivier, B. ; Arnold, M. ; Yiou, P. ; Blamart, D. ; Raynaud, S. (2010). Variability of the northeast Atlantic sea surface  $\Delta^{14}$ C and the North Atlantic Oscillation (NAO). *Quaternary Science Reviews*, 29, 2633-2646.
- Vargas, J.M.; García-Lafuente, J.; Delgado, J; Criado, F. (2003). Seasonal and wind-induced variability of Sea Surface Temperature patterns in the Gulf of Cádiz. *Journal of Marine Systems*, 38, 205-219.