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The conversion into calendar dates of radiocarbon ages of marine organisms collected on the Andalusian coast of the Gulf of Cadiz - the new Marine20 calibration curve

> La conversión a fechas de calendario de las edades radiocarbónicas de organismos marinos recogidos en la costa andaluza del Golfo de Cádiz: la nueva curva de calibración Marine20

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Abstract

Recently, a new calibration curve (Marine20) for marine radiocarbon dates has been published. Since the modelling carried out for its setting up, as well as the database used, are different from those used for the previous curves (Marine04, Marine09, Marine13), it becomes necessary to calculate new values of the marine reservoir effect (Δ_{20} R) for the oceanic region under study. This work precisely presents the new Δ_{20} R values for the Andalusian coast of the Gulf of Cadiz, determined using the previously published database (i.e. conventional ¹⁴C dates of pairs of coeval samples that lived in different carbon reservoirs, namely in the marine and in the terrestrial biospheres). Users of the Marine20 curve are thus provided with the most reliable values so far determined for this Atlantic coast.

Keywords: Marine reservoir effect, Coastal upwelling, Azores Front, Azores Current, Holocene.

Resumen

Recientemente se ha publicado una nueva curva de calibración (Marine20) para dataciones de radiocarbono de muestras marinas. Dado que la modelización realizada para su configuración, así como la base de datos utilizada, fueron diferentes a las empleadas para las curvas anteriores (Marine04, Marine09, Marine13), se hace necesario calcular los nuevos valores del efecto reservorio radiocarbónico marino (Δ_{50} R) para la región oceánica en estudio. Este trabajo presenta precisamente los valores de Δ_{20} R para la costa andaluza del Golfo de Cádiz, determinados utilizando la base de datos previamente publicada (datas convencionales de ¹4C de





pares de muestras coetáneas que vivieron en diferentes reservorios de carbono, concretamente en la biosfera marina y en la terrestre). De esta forma, los usuarios de la curva Marine20 disponen de los valores más fiables determinados hasta la fecha para esta costa atlántica.

Palabras clave: Efecto reservorio marino, Afloramiento costero, Frente de las Azores, Corriente de las Azores, Holoceno.

1. Introduction

If radiocarbon (14C) dates from marine biosphere samples are to be used to build up accurate and reliable absolute chronologies for a given oceanic region and/or for a given time interval or epoch, prior research is required, not only regarding the so-called marine or oceanic reservoir effect (ΔR), but also regarding the oceanographic conditions prevailing in the region under study. As is well known, the geochemical reservoir constituted by the ocean is deficient in ¹⁴C compared to the geochemical reservoir constituted by the atmosphere. Due to this deficiency in ¹⁴C there is a reservoir age for the ocean, i.e. there is a difference in ¹⁴C ages between contemporary samples of marine and terrestrial origin. This age difference, also called the ¹⁴C reservoir age - R(t) - will therefore be defined, according to Stuiver et al. (1986), as the difference between the conventional 14C dates of a pair of contemporary samples of organisms that lived in different carbon reservoirs (atmosphere and ocean). Stuiver and collaborators proposed a value of 405 14C years for the age difference between the surface layer of the global ocean and the atmosphere. They modelled the response of this surface layer to temporal variations in atmospheric ¹⁴C content using a box-diffusion model of ocean-atmosphere interaction (Oeschger et al., 1975). Over time, several calibration curves for 14C dates of marine samples built up using the same box-diffusion model have been published, namely Marine04 (Hughen et al., 2004), Marine09 (Reimer et al., 2009) and Marine13 (Reimer et al., 2013).

However, there are atmospheric and/or oceanographic phenomena on a regional and

even local scale that can cause a difference in the ¹⁴C content of the regional surface seawater and the surface seawater of the ocean as a whole. One of these phenomena is the occurrence of upwelling (or coastal upwelling), which consists on the coming to the surface of deep waters that are more deficient in ¹⁴C than surface waters. Upwelling is a regional phenomenon, the intensity of which varies from region to region. Taking into account this fact or other specific features from a given oceanographic region, a parameter ΔR , the so-called reservoir effect of that oceanographic region, must be determined prior to the use of a calibration curve for ¹⁴C dates of marine samples. ΔR is thus defined as the difference between the reservoir age of the mixed layer of the oceanic region under study and the reservoir age of the mixed layer of the ocean considered as a whole.

In regions with active upwelling, the intensity of this phenomenon, which is a wind-driven process, can vary over time, so it is predictable that the values of ΔR may also vary over time. Along the western Atlantic coasts of Europe coastal upwelling has shown significant activity during the Holocene only on the coasts of the Iberian Peninsula, particularly between Cape Finisterre and Cape S. Vincente, and although with less intensity along the Barlavento (windward) coast of the Algarve, appearing sporadically on the Sotavento (leeward) coast. Research on the marine reservoir effect in the Atlantic coast of the Iberian Peninsula, taking into account not only its variability along time and region, but also its correlation with Iberian coastal upwelling and climatic change, has allowed some synthesis on the phenomenon and, consequently, on the marine reservoir effect (Martins, 2014; Martins and Soares,

2013; Soares, 1993, 2005, 2010, 2011, 2015; Soares and Dias, 2006a, 2006b, 2007; Soares and Martins, 2009, 2010; Soares *et al.*, 2016). The quantification of ΔR is of crucial importance for the correct calibration of ¹⁴C ages of marine samples. Moreover, the results of previous research have shown a good correlation between ΔR values and the oceanographic conditions present in the corresponding regions.

The western Portuguese coast, which stretches from the mouth of the River Minho to the Cape S. Vicente (Figure 1), is characterized by an intense upwelling phenomenon. The weighted mean of the ΔR values determined, either with historically dated marine shells (modern value) or with pairs of archaeological samples, are in agreement with the current state of knowledge about the intensity and frequency of the upwelling phenomenon in this stretch of coast: high values of ΔR $(\Delta_{13}R_{modern}^{}$ =+250±25 ^{14}C yr) in accordance with an intense upwelling nowadays and a mean value of $\Delta_{13}R$ of +95±15 ^{14}C yr for the time interval between 3000 to 600 BP, suggesting a significant fluctuation with time in the strength of the phenomenon (Soares and Dias, 2006b).

The western stretch of the southern Iberian Atlantic coast, the so-called Barlavento region of Algarve, located between Cape S. Vicente and Cape Santa Maria (Figure 1), is influenced by the dynamic effect of Cape S. Vicente, which allows the upwelled water present along the western Portuguese coast to move southeastward and eastward, creating a quasi-permanent upwelling area around the cape. A Δ_{13} R weighted mean value of +69±17 ¹⁴C yr was determined in previous research for this coastal region, which is consistent with the prevailing oceanographic conditions (Soares, 2015).

The central part of the southern Iberian Atlantic coast, the Sotavento region of Algarve, located between Cape Santa Maria and the mouth of the River Guadiana (Figure 1), shows a minor upwelling area offshore to the

east of Cape Santa Maria when the prevailing winds in the Gulf of Cadiz are from west. A $\Delta_{13}R$ weighted mean value of -26±14 ^{14}C yr was determined, which is also consistent with the prevailing oceanographic conditions (Soares, 2015).

In the eastern region of the southern Iberian Atlantic coast, the Andalusian coast (Figure 1), the wind-driven coastal upwelling is nonexistent due to the configuration of this coast. A Δ_{13} R weighted mean value of -108±31 14 C yr was determined in previous research, which is consistent with an absent coastal upwelling, suggesting some stratification of the water column (Soares, 2015).

The Sotavento coastal region can therefore be considered as a transition zone between an area where upwelled waters are important, due to the influence of the western coastal upwelling system, and an area where a wind-driven coastal upwelling regime is nonexistent. The ΔR values mentioned above determined for the three regions are consequently in accordance with the prevailing oceanographic conditions. Positive $\Delta_{13}R$ values can be correlated with a strong upwelling, while low or very negative values correspond to a weak or even nonexistent upwelling. As a measure of the regional enhancement or depletion of ¹⁴C, the parameter ΔR can also be used as an upwelling proxy providing a significant signal of the upwelling activity (Diffenbaugh *et al.*, 2003).

2. The new Marine20 calibration curve

A new calibration curve for ¹⁴C dates of marine samples was recently published - Marine20 (Heaton *et al.*, 2020). Unlike the calibration curves mentioned above, the modelling used to build up this latest curve did not use a "box-diffusion" model, but rather a more robust model, the BICYCLE model, which, in addition to considering the variability of ¹⁴C content in the atmosphere, also incorporates time-dependent variations in the global carbon cycle. As a result of these changes, the

value obtained with the Marine20 curve for any ΔR ($\Delta_{20}R$) differs by more than one hundred ¹⁴C years from that calculated with the Marine13 curve ($\Delta_{1,2}R$), the difference being approximately -150 ¹⁴C years at 0 cal BP (Heaton et al., 2022, Fig. 1). It should also be noted that the calibration of radiocarbon dates from marine samples using either the Marine13 or Marine20 curves leads to non-significantly different results for Holocene samples, provided that the respective ΔR values are used. However, this is only valid for ages between 10500 cal BP and the present, but is not the case for the time interval 55000 - 10500 cal BP, nor for samples from the polar regions older than 11.5 ka cal BP (Heaton et al., 2022, Fig. 1). Furthermore, instead of the value of 405 14C years for the age difference, between

the surface layer of the global ocean and the atmosphere, used in the "box-diffusion" model for the Marine13, a mean value of 585 ¹⁴C years would better fit the difference between the ages of the samples from the two geochemical reservoirs when using the Marine20 curve (Heaton *et al.*, 2020, Figs. 9A and 9B; 2022, p. 259).

Thus, for a reliable and accurate use of the Marine20 curve it is necessary to calculate the $\Delta_{20}R$ values, since the use of the $\Delta_{13}R$ values with the new calibration curve leads to calibrated dates (calendar dates) with significant errors. To estimate the $\Delta_{20}R$ values from the ^{14}C dating of a coeval pair of samples from the terrestrial biosphere and the marine biosphere or from the ^{14}C date of a historically dated sample from the marine biosphere,



Figure 1: Location of the coastal regions analysed and sampled archaeological sites referred in Table 1. Archaeological sites: 1- Papa Uvas; 2 - El Eucaliptal; 3 - Niebla; 4 - La Viña.

Figura 1: Situación de los sectores costeros analizados y sitios arqueológicos muestreados citados en la Tabla 1. Sitios arqueológicos: 1- Papa Uvas; 2 - El Eucaliptal; 3 - Niebla; 4 - La Viña.

the process/calculation provided by the link http://calib.org/marine/ can be used (Reimer and Reimer, 2017).

The $\Delta_{20}R$ values determined for the western Portuguese coast as well as for the southern coast of Algarve have already been published (Soares and Valério, 2023-2024, Quadro 8, Fig. 2). The calculated mean Δ_{20} R values, using pairs of archaeological samples, are as follows: Western coast Δ_{20} R= -100±17 ¹⁴C yr (Δ_{13} R= +95±15 14 C yr), Barlavento coast Δ_{20} R= -118±14 14 C yr (Δ_{13} R= + 69±17 14 C yr) and Sotavento coast Δ_{20} R= -192±14 ¹⁴C yr (Δ_{13} R= -26±14 ¹⁴C yr). It can then be noted that a strong upwelling can be correlated with positive $\Delta_{13}R$ values or with $\Delta_{20}R$ values higher than -150 ^{14}C yr, while a weak or nonexistent upwelling correspond to low or negative values of $\Delta_{13}R$ or to $\Delta_{20}R$ values lower than -150 ¹⁴C yr.

It is therefore advisable to use the Marine20 curve since this new curve was built up from a more robust database and modelling, also considering a greater number of variables that contribute to the variability of the ¹⁴C deficiency of the surface layer of the ocean over time.

3. Material and methods

3.1. Sampling

Pairs of closely associated archaeological samples (marine shells/bones) collected from a series of Andalusian archaeological sites (Fig. 1), namely from Neolithic contexts of Papa Uvas (Soares and Martin de la Cruz, 1995), Late Neolithic/Early Chalcolithic contexts of La Viña (Ruiz Gil and Ruiz Fernández, 1987; Ruiz Fernández and Ruiz Gil, 1989), also from a Roman environment at El Eucaliptal (Campos Carrasco et al., 1999b) and from the Historic Center of Niebla (Campos Carrasco et al., 1999a, 2001; Pérez Macías et al., 1997) were radiocarbon dated. Each pair was collected from the same level in a restricted area that corresponds to a well defined archaeological context. A detailed description of the samples (mammal bones and marine shells) can be found in Soares (2005, pp. 142-149).

3.2. Experimental and data processing

Analytical procedures are also described elsewhere (Soares, 2005, Soares and Dias, 2006, 2007). Radiocarbon dates were calculated in accordance with the definitions recommended by Stuiver and Polach (1977). $\Delta_{20}R$ values were determined using the link http://calib. org/marine/ as mentioned above, i.e. converting the ^{14}C date of the terrestrial sample into a marine model age, which is then subtracted from the associated marine shell ^{14}C age to yield $\Delta_{20}R$.

4. Calibration of radiocarbon dates of marine samples collected on the Andalusian coast of the Gulf of Cadiz

4.1. Results

Table 1 presents all the data carried for this work, including the weighted average of the Δ_{20} R values determined for the nine pairs of closely associated samples from the four archaeological sites mentioned above. Each pair, terrestrial and marine, was recorded from a specific archaeological context radiocarbon dated using both samples, which were distributed over the time interval 4600 - 200 BP (terrestrial samples). The calibrated ages presented in this table correspond to those determined with the respective terrestrial samples using the IntCal20 curve (Reimer et al., 2020). The $\Delta_{13}R$ values obtained with the Marine13 curve (see Soares, 2015, Table 1) are also shown, in order to get an easier comparison between the values obtained for the marine reservoir effect on the Andalusian Atlantic coast with the two quantifications. The bibliographic references in Table 1 are those where the dated archaeological contexts are described and interpreted.

4.2. Discussion and final remarks

The high Δ_{20} R values (Δ_{20} R> -150 14 C yr) or the positive values of Δ_{13} R determined for the interval 4400-4000 BP seem to be consistent with a strong upwelling. The inception of this

phenomenon was probably not related to the intensity and the direction of the wind prevailing in the coastal region, but more likely to the position of the Azores Front. A similar situation has been identified in two periods between the Last Glacial Maximum and the Holocene, i.e. just prior to 16 ka BP and during the Younger Dryas, 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).

Figure 2 presents graphically, as a function of time, the values of $\Delta_{20}R$ determined for the southern Atlantic coast of the Iberian Peninsula. To make easier to read and compare the three diagrams, and taking into account

the comparison with the values obtained with the previous calibration curves (see, for example, Soares, 2011, Figs. 1-4; 2015, Fig. 2; Soares and Valério, 2023-2024, Fig. .2), the abscissa axis is anchored to the ordinate axis for $\Delta_{20}R$ = -150 ^{14}C yr, since this is approximately the difference, as mentioned above, between the ΔR values calculated with Marine 20 and those calculated with the previous curves, notably with Marine13. We will not detail here the inferences that can be drawn from them, since the use of the Marine20 curve does not modify those that were drawn with the previous calibration curves and have already been published (see, for example, Soares, 2011, 2015; Soares & Dias, 2006a; Soares and Valério, 2023-2024).

Table 1: Δ_{20} R and Δ_{13} R for the Andalusian coast of the Gulf of Cadiz. Tabla 1: Δ_{20} R y Δ_{13} R para la costa andaluza del Golfo de Cádiz.

Archaeological		¹⁴ C age (BP)	¹⁴ C age (BP)		Δ ₁₃ R	Δ ₂₀ R	
context		(terrestrial)	(marine)	cal BP (2σ)	(14C yr)	(14C yr)	Bibliography
Papa Uvas	E15	4574±108	4820±70	5573-4882	-117±114	-297±158	Soares and Martin de la Cruz, 1995
Papa Uvas	FIV	4475±49	4760±55	5307-4887	-103±80	-262±96	Soares and Martin de la Cruz, 1995
La Viña	Silo 16	4428±83	4960±40	5294-4859	+200±66	-9±116	Ruiz Gil and Ruiz Fernández, 1987; Ruiz Fernández and Ruiz Gil, 1989
Papa Uvas	F12	4421±94	4850±70	5304-4848	+98±106	-115±133	Soares and Martin de la Cruz, 1995
Papa Uvas	B10	4054±195	4740±50	5211-3931	+327±233	+170±214	Soares and Martin de la Cruz, 1995
Niebla	UE69	2067±65	2240±80	2299-1831	-163±105	-302±113	Campos Carrasco et al., 2001
El Eucaliptal	UE4	1751±84	1960±30	1862-1414	-142±73	-265±84	Campos Carrasco et al., 1999b
Niebla	UE16	904±40	1180±70	911-732	-82±77	-263±87	Campos Carrasco et al., 1999a
Niebla	SA/V	218±43	550±40	425-1	-88±54	-246±168	Pérez Macías et al., 1997
Weighted Mean Calculation for Δ ₂₀ R							

Weighted Mean Calculation for $\Delta_{20}R$ (all $\Delta_{20}R$ values) Teste $X^2_{0.05}$ T = 8.75 ($X^2_{0.05}$ = 15.51)

Weighted Mean: $\Delta_{20}R = -216 \pm 38^{14}C$ yr

Weighted Mean Calculation for $\Delta_{20}R$

 $(\Delta_{20}R \text{ values} < -150^{14}C \text{ yr})$ Teste $X^{2}_{0.05}T$ $T = 0.15 (X^{2}_{0.05} = 11.07)$

Weighted Mean: $\Delta_{20}R = -270 \pm 43^{14}C$ yr

Weighted Mean Calculation for $\Delta_{20}R$

 $(\Delta_{20}R \ values > -150^{14}C \ yr)$ Teste $X_{0.05}^2 \ T$ T = 1.31 ($X_{0.05}^2 = 5.99$)

Weighted Mean: $\Delta_{20}R = -23 \pm 81^{-14}C$ yr

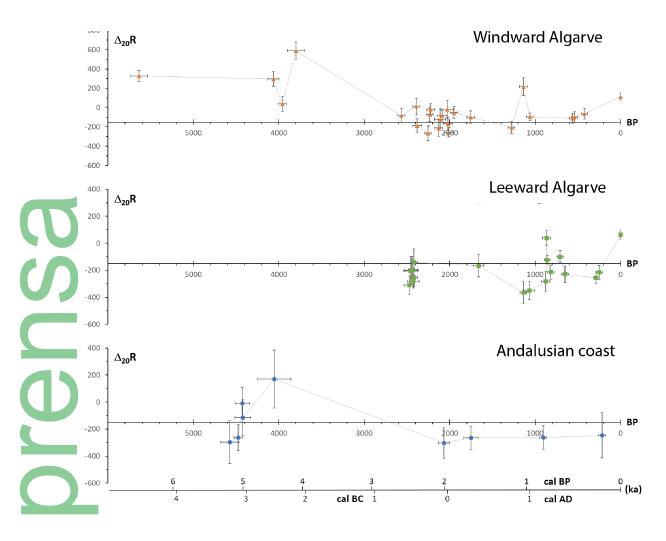


Figure 2: $\Delta_{20}R$ (±1 σ) values for the 3 coastal regions plotted versus terrestrial 14C ages (±1 σ) (Algarve data following Soares and Valério, 2023-2024).

Figura 2: Valores de $\Delta_{20}R$ ($\pm 1\sigma$) de los tres sectores costeros, comparados con edades de 14C ($\pm 1\sigma$) terrestre (datos del Algarve siguiendo a Soares y Valério, 2023-2024).

The use of a more accurate modelling in this work does not modify these inferences, notably those referring to the behaviour of the upwelling phenomenon on the northern coast of the Gulf of Cádiz, but makes them more reliable. In any case, we would like to emphasize that the effect of the oceanic reservoir or the age of the oceanic reservoir, as we wish to call it, in the three stretches of the Atlantic coast under study, and likewise the intensity of coastal upwelling, have varied over time. The weighted averages of the $\Delta_{20}R$ values determined either with histori-

cally dated shells or with pairs of archaeological samples (as we did in this work, which is now published) are in agreement with the current state of knowledge about the intensity and frequency of the upwelling phenomenon in the three marked coastal stretches: high values (many of them positive) of $\Delta_{\rm 20}R$ in the Barlavento Coast, in accordance with an intense upwelling; lower values in the Sotavento, corresponding to a less intense and infrequent upwelling; and the lowest values in the Andalusian Atlantic coast, where the coastal upwelling is absent.

It is also worth highlighting the set of high $\Delta_{20}R$ values determined for marine shells from the Andalusian coast of the Gulf of Cadiz with an age between approximately 4400 - 4000 BP. A similar situation was also determined for the Barlavento coast of Algarve, apparently for a period of time around 4000 BP (Soares, 2011; Martins & Soares, 2013, Soares and Valério, 2023-2024). These situations are therefore correlated with a very intense upwelling that would have occurred at that time in the Gulf of Cadiz, which would be explained by the extension of the Azores Front in an easterly direction along the Azores Current up to the Pillars of Hercules, as would have happened in two time intervals situated between the Last Glacial Maximum and the Holocene (Rogerson et al., 2004). On the other hand, as referred to above, due to the configuration of the Andalusian coastline of the Gulf of Cadiz the wind-driven coastal upwelling is nonexistent in this coastal region, and the low $\Delta_{20}R$ values (Δ_{20} R weighted mean=-270±43 ¹⁴C yr) determined for the interval 2000-200 BP or around 4500 BP agree with this fact.

Finally, it should be taken into account, that although weighted mean values have been calculated, it is recommended, when calibrating ¹⁴C dates of marine organisms from a given context (see Heaton et al., 2022, pp. 252-254), to use the values already determined for geographically closed contexts and, if possible, also chronologically closed ones. If these conditions are not met, then the weighted mean value for the stretch of coast where the context to be dated is located should be used. Nevertheless, the available data introduce some uncertainty when performing the calibration of conventional 14C dates of marine shells from the 5th millennium BP collected in the Andalusian coast, namely if the ¹⁴C date is between 4600 and 4400 BP. Table 1 shows that the first four ¹⁴C dates (Papa Uvas E15, Papa Uvas FIV, La Viña Silo 16, and Papa Uvas F12) are statistically indistinguishable at 2σ level (T=1.46; $(X_{0.05}^2 = 7.81)$. But to the first two ¹⁴C dates corresponds a Δ_{20} R=-270±43 ¹⁴C yr, while to the other two a $\tilde{\Delta}_{20}$ R=-23±81 ¹⁴C yr. So, a priori,

we do not know which $\Delta_{20}R$ we must use for the calibration of a new ^{14}C date with a value between 4400-4600 BP. If this date is from a sequence of dates and we are using a Bayesian model it will perhaps be possible to choose one of the $\Delta_{20}R$ weighted mean values taking into account the value obtained for the model agreement. For other cases using marine shell dates from the 5th millennium BP associated to the Andalusian coast it will be hard to choose which of the two $\Delta_{20}R$ weighted mean values should be used.

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