

Revisiting the marine reservoir age in Baja California continental margin sediments using ^{14}C and ^{210}Pb dating



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ABSTRACT

Knowledge of the Marine Reservoir Effect (MRE) correction is fundamental in palaeoceanographic research to establish an accurate age-depth model for marine sedimentary records. However, during the last decades different MRE corrections have been applied in inconsistent ways for the same locality and same sediment cores, at Soledad Basin, Baja California, Mexico, creating confusion about the proper correction value of the marine reservoir effect (ΔR) to be applied. In contrast with the empirical approach previously used for assessing the ΔR value in Soledad Basin, in this study we applied an analytical approach based on the concurrent application of AMS- ^{14}C and $^{210}\text{Pb}_{\text{xs}}$ dating techniques made on sedimentary total organic carbon and foraminifera to determine new regional ΔR values from newly collected sediment cores from this site. Our results from Soledad Basin show a ΔR of 206 ± 32 years for foraminifera and 706 ± 42 years for organic carbon. Modeled ages using these results, and compared with those previously applied for the basin, highlight the relevance of the correct use of the local reservoir age as it can generate an offset of approximately 150 years if the other published ΔR were used. These differences can shift core chronologies by several decades and thus yield significant errors in palaeoceanographic reconstructions, which will be important to remedy in future work.

1. Introduction

Marine sediment cores are among the most commonly used paleoclimate archives. During the last decades, the methodological approaches to study them have become highly diversified, enabling advances in reconstructing physical and chemical processes that have occurred during recent Earth history (Hillaire-Marcel and de Vernal, 2007). The information extracted from these records is highly relevant for future climate projections. In particular, sedimentary archives of the last two millennia have provided insights into natural variability of climatic states occurring on multi-decadal time scales which are not adequately represented by the instrumental record that extends back to about 1850 (Masson-Delmotte et al., 2013; PAGES2k Consortium, 2017; Turney et al., 2019). One of the essential prerequisites for comparing high-resolution palaeoceanographic reconstructions of the Common Era (CE) is the need to convert sediment depths into ages through the establishment of robust and precise chronostratigraphies. Radiocarbon

dating is the most employed method for developing age models of Holocene marine sedimentary records. Nevertheless, this method requires the precise correction of ^{14}C dates to obtain an accurate age-depth model.

In the ocean, the ^{14}C ages of materials produced in the surface are older than ^{14}C ages of contemporaneous terrestrial materials, as the result of mixing the upper water column with older, deeper water (Broecker, 1991; Stuiver and Braziunas, 1993). This difference is referred to as the marine “reservoir age” (R) (Stuiver and Polach, 1977; Stuiver et al., 1986; Stuiver and Braziunas, 1993), and for the pre-nuclear weapons testing era is “globally” assumed to be ~ 400 years by convention (Reimer et al., 2013). This discrepancy can be corrected by subtracting R from the conventional marine ^{14}C ages measured in marine samples. However, the ocean is heterogeneous and surface mixing rates vary in space and time, especially in upwelling regions, leading to deviations of local ^{14}C ages from the average global reservoir value (e.g., Kennett et al., 1997; Bondevik et al., 2006; Ortlieb et al.,

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2011). The regional deviation, known as ΔR or the marine reservoir effect (MRE), is, therefore, the difference between the radiocarbon age measured in a marine sample and the global marine reservoir age (Stuiver et al., 1986; Stuiver and Braziunas, 1993). Consequently, to achieve precise chronostratigraphy of marine sedimentary records, it is essential to have an accurate knowledge of the regional ΔR .

Commonly, the ΔR value for a specific site is obtained from the Marine Reservoir Database (Reimer and Reimer, 2001; <http://calib.org/marine/>), and when not available, ΔR values from a nearby region have been used, in spite of the potential errors that would result if the oceanographic characteristics of the site are distinct (Hinojosa et al., 2015). This presents challenges with regard to the choice of ΔR value used, especially when various published studies at the same site have used different ΔR values to establish their respective age models. This is the case for Soledad Basin (also known as San Lázaro Basin) located at the Baja California's continental margin where, recently, two high-resolution palaeoceanographic studies spanning the last 2 millennia were published using two independent reconstructions of sea-surface conditions for the same marine sediment core: 1) alkenones (O'Mara et al., 2019) and 2) Mg/Ca of planktic foraminifera (Abella-Gutiérrez et al., 2020). These authors used the same ^{14}C results but ΔR values that differed by approximately 100 years. This choice has profound implications for the interpretations of both palaeoceanographic studies, especially since it has been shown that a difference of 100 years in ΔR corrections applied to the same conventional ^{14}C age affects the calibrated age by several decades (Alves et al., 2018). Therefore, care must be taken when developing an age model because improper choice of the ΔR value may create a time-shift in the reconstructions of environmental conditions, and thus a misinterpretation of paleorecords, especially at decadal to multi-decadal time scales.

To date, the publication record for Soledad Basin has used four different ΔR values, yielding inconsistent reconstructed histories of environmental variability. Thus, this study aims to (1) determine an accurate local reservoir age using an alternative dating method ($^{210}\text{Pb}_{\text{xs}}$) and, (2) establish a reliable chronology on newly collected sediment cores from Soledad Basin to compare with published regional ΔR values.

2. Sampling site and local ΔR values

Soledad Basin is located in the Eastern Tropical North Pacific, on the Mexican continental slope off Southern Baja California, 50 km off the coast (Fig. 1). The basin is a NW-SE elongated bathymetric depression with a maximum depth of 550 m. This semi-closed basin, with a sill depth of 290 m, limits the advection of deeper water masses, thus

restraining the oxygenation of the basin and creating sub-oxic to anoxic conditions, inhibiting bioturbation and allowing the preservation of coarse laminated sediments (van Geen et al., 2003). Terrestrial influence is considered unimportant in the region mainly due to the absence of rivers and the very low precipitation inland, characterized by a mean annual precipitation of ~ 10 mm (Fig. 1; data from clicom-mex.cicese.mx). Studies on surface sediments have shown that the organic material exported into Soledad Basin is mainly of marine origin (Carriquiry et al., 2003).

The hydrography of the study area is controlled by the influence of cold and well-oxygenated sub-Arctic surface water flowing equatorward during winter-spring (California Current: 0–200 m), and warmer, saltier and less-oxygenated subsurface waters (California Undercurrent: 100–300 m) flowing poleward from summer to autumn (Durazo, 2015). The seasonality is driven by the strengthening of the northwesterly winds, promoting upwelling in the region (Zaytsev et al., 2003). This southern limb component of the California Current System is thus characterized by a season of strong upwelling with high productivity from February to July, and a second faint and/or warm season of low productivity from August to January (Cervantes-Duarte et al., 2015).

Upwelled deep water is low in ^{14}C content, explaining the significant deviation of the regional marine reservoir signature from the global marine reservoir age (Berger et al., 1966; Ingram and Sounth, 1996). Berger et al. (1966) originally estimated a ΔR of 201 ± 53 years based on ^{14}C measurement of a known-age mollusk shell collected in Magdalena Bay, located 102 km from Soledad (Fig. 1). This ΔR value was modified then by Stuiver and Braziunas (1993) to 235 ± 35 years for the coast of California. Later palaeoceanographic studies on sediment cores collected in Soledad Basin (our study site) have applied different ΔR values to establish the chronostratigraphy for their records. For example, van Geen et al. (2003) used a ΔR value of 200 ± 100 years, but recently O'Mara et al. (2019) used a ΔR of 253 ± 122 years by averaging the ΔR of Cedros Island and Cabo San Lucas (which had been determined by Berger et al., 1966). The most recent chronostratigraphy from this site, however, used a ΔR value of 350 ± 50 years (Abella-Gutiérrez et al., 2020), as a result of increasing by 100 years the reservoir age of 650 years proposed by Abella-Gutiérrez and Herguera (2016).

3. Materials and methods

3.1. Sediment cores: collection and characteristics

Three sediment cores were collected at the same location from the Soledad Basin (Fig. 1), on the continental shelf off southwest Baja

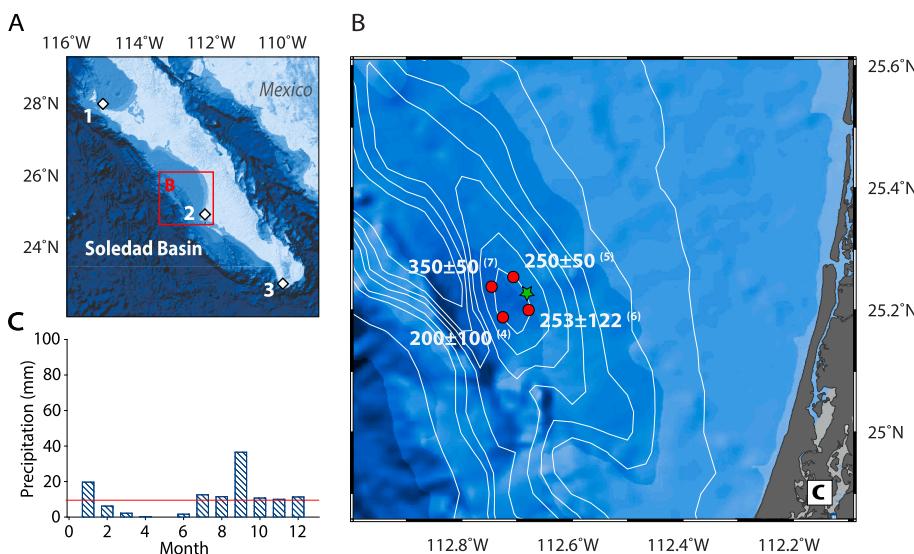


Fig. 1. (A) Map of the Baja California Peninsula, Mexico, showing the study area and the position of local reservoir ages obtained in the Marine Reservoir Database and published in Berger et al. (1966) (white diamonds): 1- Cedros Island, $\Delta R = 155 \pm 51$ years; 2- Magdalena Bay, $\Delta R = 201 \pm 53$ years; 3- Cabo San Lucas, $\Delta R = 329 \pm 45$ years. (B) Inset map of Soledad Basin region with bathymetry, showing the location of the nearest meteorological station in the mainland (C); the marine sediment composite core RR18-SOL-MC1/SD6-MC/GC2 (green star, this study); and the ΔR values used in nearby cores cited in this paper (4- van Geen et al., 2003; 5- Abella-Gutiérrez and Herguera, 2016; 6- O'Mara et al., 2019; 7- Abella-Gutiérrez et al., 2020). (C) Histogram of mean monthly precipitation; the mean annual precipitation (red line) corresponds to 10 mm. This figure was partly produced with Ocean Data View (Schlitzer, 2015) and QGIS (<https://www.qgis.org>).

California ($25^{\circ}11.99'N$; $112^{\circ}43.99'W$; 550 m water depth) in 2012 on the R/V Thomas G. Thompson (multicore SD-6-MC and gravity core SD-6-GC2) and in 2018 on the R/V Roger Revelle (multicore RR18-SOL-MC1). The multicores were collected to overlap with gravity core SD-6-GC2, providing intact, undisturbed core tops that otherwise could be disturbed during gravity coring. The use of a multicorer ensures the recovery of undisturbed surface sediment (Barnett et al., 1984).

After a visual inspection to check that there is no sediment resuspension, multicore RR18-SOL-MC1 was carefully sliced on board at 0.3 cm intervals immediately after retrieval, while sediment cores SD-6-MC and SD-6-GC2 were sampled in the laboratory at 0.25 cm intervals. Dry bulk density (DBD) and porosity were measured on RR18-SOL-MC1 by determining the weight after freeze-drying of a known volume of wet sediment.

Generally, unconsolidated surface sediments suffer physical compaction caused by transport and sampling. This induces a vertical displacement of the cored sediments with respect to their natural position, resulting in underestimated sedimentation rates (Morton and White, 1997). Since multicore RR18-SOL-MC1 was sampled immediately after retrieval, we explicitly assume its top stratigraphic structure is better suited than SD-6-MC and SD-6-GC2 sediment cores for establishing more precise chronologies. Cores SD-6-MC and SD-6-GC2 were ^{14}C -dated and Total Organic Carbon (TOC) (%) was measured. TOC content in both cores SD-6-MC/GC2 was compared and used to adjust their stratigraphic structure based on the chronology of the TOC measured in multicore RR18-SOL-MC1. TOC content was determined by acid treatment of freeze-dried sediment samples, in order to remove inorganic carbon (e.g., $CaCO_3$), and was analyzed in a Thermo Fisher Flash 2000HT elemental analyzer. The internal reproducibility of the measurements was assessed by using calibrated internal laboratory standards and the precision was better than $\pm 0.3\%$. Afterwards, because the cores were collected at the same site but in different years, we synchronized the cores by graphically correlating (i.e., tie points) the TOC content variations of both cores SD-6-MC/GC2 with that of core RR18-SOL-MC1 (Figure S1), aided by the QAnalySeries Software (Kotov and Pälike, 2018).

3.2. Lead-210 and radiocarbon dating

An age-depth model for the composite depth scale was developed using a combination of radiometric methods: $^{210}Pb_{xs}$ activity profiles on RR18-SOL-MC1 and SD-6-GC2 as well as AMS radiocarbon dating of planktonic foraminifera and bulk organic matter on SD-6-MC/GC2.

Activities of ^{210}Pb , ^{226}Ra , ^{228}Th and ^{137}Cs were measured in core RR18-SOL-MC1 on dry sediments by non-destructive gamma spectrometry using a low background, high efficiency, well-shaped detector (CANBERRA) (Schmidt et al., 2014) at the University of Bordeaux. Calibration of the detector was achieved using certified reference material (IAEA-RGU-1, -RGTh-1, and -135). Activities are expressed in $mBq.g^{-1}$ and errors are based on 1 standard deviation counting statistics. Excess ^{210}Pb and ^{228}Th ($^{210}Pb_{xs}$; $^{228}Th_{xs}$) were calculated by subtracting the activity supported by their respective parent isotopes, ^{226}Ra and ^{228}Ra , from the total ^{210}Pb and ^{228}Th activities in the sediment. Errors in $^{210}Pb_{xs}$ and $^{228}Th_{xs}$ were calculated by propagation of errors in the corresponding pair (^{210}Pb and ^{226}Ra ; ^{228}Th and ^{228}Ra). The $^{210}Pb_{xs}$ activity was also measured in the core top of SD-6-GC2 and compared with $^{210}Pb_{xs}$ of the multicore RR18-SOL-MC1.

The AMS radiocarbon dates on both SD-6-MC and SD-6-GC2 cores were measured at two laboratories, the Keck Carbon Cycle AMS Facility, Earth System Science department at University of California, Irvine, USA (KCCAMS/UCI); as well as the US National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at the Woods Hole Oceanographic Institution (WHOI; MA, USA). The AMS ^{14}C dates were obtained on 6 samples of mixed planktonic foraminifera and 7 samples of bulk organic matter (bulk-OM) when the sediment did not contain sufficient foraminifera (Table 1).

Table 1

AMS radiocarbon measurements for cores SD-6-MC and GC. Abbreviations: UCIAMS: UC-Irvine Keck Carbon Cycle AMS facility; NOSAMS: US NSF National Ocean Sciences AMS facility at Woods Hole Oceanographic Institution; bulk-OM: bulk organic matter; Plk. Foram.: mixed planktonic foraminifera; N/A: Not available.

Laboratory code	Sample name	Core name	Material	Composite depth (cm)	Conventional radiocarbon age (BP)
UCIAMS-140895	ST-6-SD-MC-10	SD-6-MC	bulk-OM	15.4	1170 ± 20
NOSAMS 135345	SD6-15.5	SD-6-MC	Plk. Foram.	21.7	660 ± 15
NOSAMS 135340	SD6-19.5	SD-6-MC	Plk. Foram.	26.7	710 ± 15
UCIAMS-140896	ST-6-SD-MC-30	SD-6-MC	bulk-OM	39.6	1240 ± 20
NOSAMS 135342	SD6-30.5	SD-6-MC	Plk. Foram.	39.6	745 ± 20
NOSAMS 135343	SD6-34.5	SD-6-MC	Plk. Foram.	44.0	770 ± 15
NOSAMS 135344	SD6-39.5	SD-6-MC	Plk. Foram.	49.4	885 ± 15
UCIAMS-140900	ST6GC-51	SD-6-GC	bulk-OM	51.8	1360 ± 20
UCIAMS-140901	SOL2T-40	SD-6-GC	bulk-OM	101.5	1915 ± 20
UCIAMS-140902	SOL2T-90	SD-6-GC	bulk-OM	136.5	2380 ± 20
UCIAMS-140903	SOL2B-125	SD-6-GC	bulk-OM	181.5	2870 ± 20
UCIAMS-140904	SOL2B-170	SD-6-GC	bulk-OM	226.5	3510 ± 20
UCIAMS-114696	Sol2BS-7	SD-6-GC	Plk. Foram.	296.0	4665 ± 15

4. Results and discussion

4.1. Modern sediment and mass accumulation rates

Occurrence of $^{228}Th_{xs}$ ($T_{1/2} = 1.9$ years) in the uppermost horizons of core RR18-SOL-MC1, and its rapid disappearance within the first centimeter, demonstrates the presence of freshly deposited material at

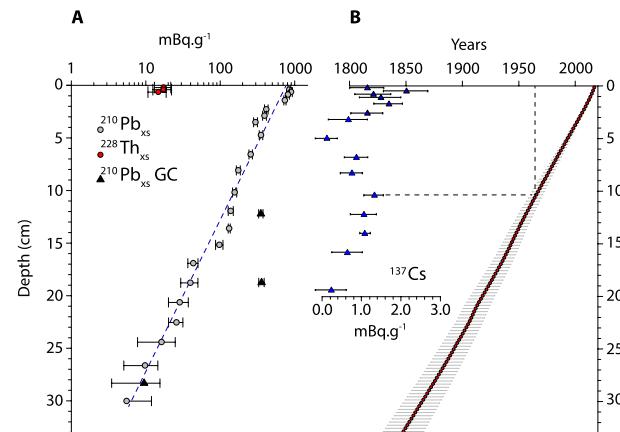


Fig. 2. (A) Integrated mass profile of $^{210}Pb_{xs}$ (grey circles) and $^{228}Th_{xs}$ (red circles) activities in core RR18-SOL-MC1 and $^{210}Pb_{xs}$ activity in core SD-6-GC (black triangles) with one sigma error bars; (B) ^{137}Cs activity profile and ^{210}Pb derived age model against sediment depth.

the core top and a very low bioturbation rate (Fig. 2A). The longer-term $^{210}\text{Pb}_{\text{xs}}$ ($T_{1/2} = 22.3$ years) presents a more deeper penetration in the sedimentary column, with detectable activity at depths deeper than 30 cm.

Several models exist to calculate age from $^{210}\text{Pb}_{\text{xs}}$ according to the hypothesis formulated on $^{210}\text{Pb}_{\text{xs}}$ concentration in sediment, its flux to the sediment surface and mass accumulation rate (Appleby and Oldfield, 1978; Robbins, 1978; Sanchez-Cabeza and Ruiz-Fernández, 2012). The $^{210}\text{Pb}_{\text{xs}}$ profile in core RR18-SOL-MC1 displays a regular exponential decrease with integrated dry mass (Fig. 2A; determination coefficient of 0.98), allowing the assumption that ^{210}Pb activity of freshly-deposited sediment is constant over time and thus correctly applying the Constant Flux Constant Sedimentation model. In practice, Mass Accumulation Rate (MAR) was estimated from the decrease of $^{210}\text{Pb}_{\text{xs}}$ versus integrated dry mass (Figure S2). The calculated MAR is $60 \pm 6 \text{ mg cm}^{-2} \cdot \text{yr}^{-1}$, in agreement with the MAR estimated in a previous study on a sediment multicore collected in the same area ($77 \pm 11 \text{ mg cm}^{-2} \cdot \text{yr}^{-1}$; Deutsch et al., 2014). The deposition time of each sediment layer was obtained by dividing the cumulated dry mass per unit area by the MAR. The deposition year was subsequently calculated assuming the age of the top core to be 2018, the year of the core collection. The ^{210}Pb chronology indicates that the multicore RR18-SOL-MC1 spans beyond the last 150 years. The onset of ^{137}Cs activity between 10 and 13.5 cm in the core corresponds to the beginning of its production during nuclear bomb testing (1950's), in agreement with our ^{210}Pb dating model (Fig. 2B).

In order to determine how much of the upper sediments of core SD-6-GC2 were conserved during the coring procedure, the $^{210}\text{Pb}_{\text{xs}}$ activity of the gravity core was compared with $^{210}\text{Pb}_{\text{xs}}$ of the multicore RR18-SOL-MC1 (Fig. 2A). Although the $^{210}\text{Pb}_{\text{xs}}$ profile of the gravity core shows at least a 10 cm section with uniform activity, corresponding certainly to mixing of the upper layers during core retrieval, the $^{210}\text{Pb}_{\text{xs}}$ activity at 16 cm from SD-6-GC2 core coincides well with that of the RR18-SOL-MC1 at around 28 cm, indicating that the top ~ 12 cm of gravity core SD-6-GC2 was lost through coring. This result is consistent with an estimated loss of ~ 11 cm from the top of the SD-6-GC2 when comparing its TOC profile with that of core RR18-SOL-MC1 (Figure S1). Finally, the ^{210}Pb age-chronology of RR18-SOL-MC1 was transferred to the upper part of the composite sequence (SD-6-MC and SD-6-GC2) by matching the TOC variations in all cores.

4.2. Regional marine ΔR estimation

The depth distribution of conventional ^{14}C ages shows a linear pattern depending on the type of the material dated: the ^{14}C ages derived from marine bulk-OM samples exhibit a consistent ^{14}C age offset of ~ 500 years relative to carbonate material (Fig. 3). AMS ^{14}C dating of organic carbon of marine origin is often needed in highly productive regions where there is scarce or poor preservation of the carbonate fraction, especially in suboxic or reducing anoxic settings such as Soledad basin (e.g., Pichevin et al., 2010). Age offsets between OM and carbonate are observed in Holocene sediments from various continental margins and have been described to be relatively constant over time (Mollenhauer et al., 2003, 2005; Ausín et al., 2019). The ~ 500 years observed age offset indicates the addition of older organic material from other processes such as advection, re-suspension, and/or fluvial discharge of pre-aged OM. The organic carbon contained in Soledad Basin sediment originates mostly from marine phytoplankton as seen in the $\delta^{13}\text{C}$ signature obtained from our analyses ($\delta^{13}\text{C} = -21.17 \pm 0.22$, $n = 1187$; *study currently in progress*) and confirmed by the isotopic composition of the settling material in a sediment trap located in Soledad Basin (Silverberg et al., 2004). Thus, fluvial discharge of pre-aged terrestrial OM is discarded as a potential process leading to age discrepancies between OM and carbonates at this locality. Since the adjacent land also consists of a desert biome region lacking any rivers or streams, lateral transport of resuspended marine material is likely responsible for supplying older OM to the sampling site, controlled mainly by physical interactions between deep water currents, sediment grains, and seafloor morphology (Mollenhauer et al., 2005). It is thus assumed in this study that the ^{14}C -age offset between OM and carbonates in Soledad Basin sediments has been constant over time, thereby allowing the estimation of a regional marine reservoir effect for each type of marine materials dated (i.e., ΔR_{foram} and ΔR_{OM}). This is supported by the relatively parallel, but consistently offset, trajectories of the OM and carbonate ^{14}C ages (Fig. 3).

Regional differences in the marine reservoir effect are generally determined through three different methods (see review in Alves et al., 2018): (1) Direct radiocarbon dating of organisms collected before 1950 years CE (pre-bomb) whose death date also is known (Known Age Marine Material method) (2) Radiocarbon dating on marine organisms (e.g., shells); and terrestrial material (e.g., charcoal), both assumed to be contemporaneous (Paired Marine/Terrestrial Samples method); and (3) Radiocarbon dating on marine samples that can also be dated with an

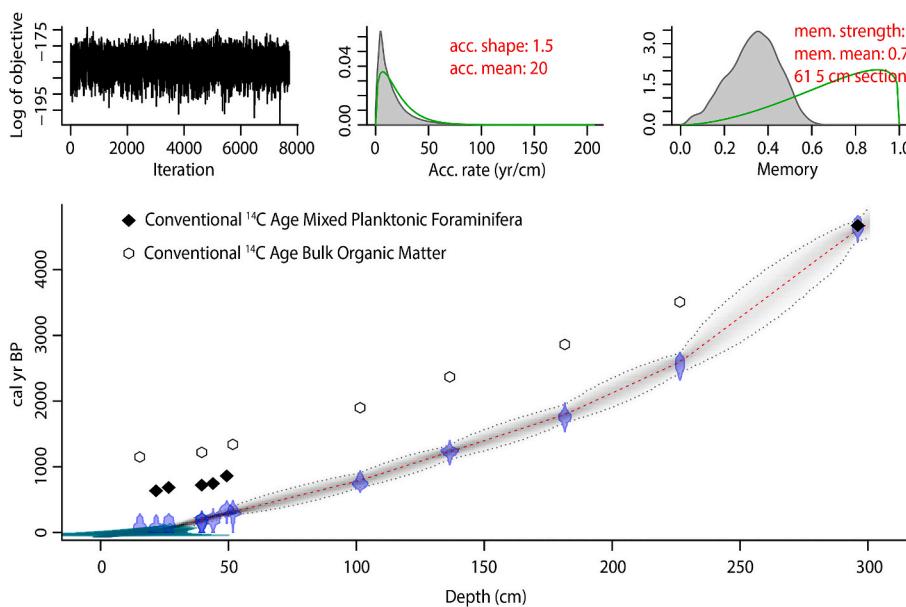


Fig. 3. Conventional ^{14}C age of mixed planktonic foraminifera (black diamonds) and bulk organic matter (white circles) plotted versus core composite depth. Also, Bacon output plot relating depth assignment to calendar years B.P., applying the local reservoir $\Delta R_{\text{foram}} = 206 \pm 32$ years and $\Delta R_{\text{OM}} = 706 \pm 42$ years assessed in this study. The ^{210}Pb model chronology is depicted in blue-green, while calibrated radiocarbon dates are presented as purple vertical shading. Possible depth-age relationships are shown in black and grey (95% C.I.), with red representing the mean age model realization. Top panels depict model parameters (green) versus data (grey) as determined by the Bacon software (Blaauw and Christen, 2011).

alternative dating method (e.g., U/Th, or tephrochronology; Paired Radiocarbon/Alternative Dating method). In this study, the last method was applied by comparing ^{14}C values (of OM and foraminifera samples) with ages also derived from the ^{210}Pb -based chronology determined at the same composite depths (Fig. 2B and Table 2). The ^{14}C age of OM at composite depth 15.4 cm is 1170 ± 20 ^{14}C years, while the calendar date is estimated at 1942 ± 8 years CE measured by ^{210}Pb chronology. The ^{14}C age of foraminifera at composite depth 21.7 cm is 660 ± 15 ^{14}C years, which corresponds to a calendar date of 1909 ± 12 years CE. Using these tie points and the online application *deltar* (Reimer and Reimer, 2017; <http://calib.org/deltar/>), ΔR_{OM} and ΔR_{foram} values were calculated to determine the ^{14}C age offsets from OM and foraminifera samples respectively (Table 2). While previous studies have used the intercept-based method in which the mean of the radiocarbon age intercepts with the calibration curve, this often underestimates the ΔR uncertainty (as seen in Sabatier et al., 2010; Russell et al., 2011): *deltar* calculates ΔR as well as the accurate uncertainty for single samples by using full probability distribution functions. In summary, the application *deltar* establishes a normal distribution with the mean and the standard deviation of the derived ^{210}Pb -derived age (converted to calendar age BP); it then reverse-calibrates discrete points on that distribution using the Marine13 calibration curve (Reimer et al., 2013) and uses a convolution integral to determine a confidence interval for the age offset between the ^{14}C -dated marine sample and the uncalibrated probability density function of the derived ^{210}Pb -derived age.

The ΔR values were thus estimated in Soledad Basin to be 706 ± 42 years and 206 ± 32 years for OM and foraminifera samples, respectively (Table 2). The local MRE calculated here for the OM fraction is the first reported for this region and confirms the constant Holocene age offset relative to foraminifera of ~ 500 years (Mollenhauer et al., 2003, 2005; Ausín et al., 2019). The ΔR_{foram} estimated in this study is consistent with the first study published for this region (Fig. 1; $\Delta R = 201 \pm 53$ years; Berger et al., 1966), as well with that of van Geen et al. (2003), but it is noticeably different from that reported recently by O'Mara et al. (2019) ($\Delta R_{\text{foram}} = 250 \pm 100$ years) and that of Abella-Gutiérrez et al. (2020) ($\Delta R_{\text{foram}} = 350$ years).

An age model was established for the composite core RR18-MC1/SD-6-MC/SD-6-GC2 using the ΔR values estimated in this study; the potential causes and implications of these discrepancies between ΔR values published for Soledad Basin are discussed next.

4.3. Soledad Basin age-depth model

The chronology of the composite multicore/gravity core was built using Bacon Software v2.4 (Blaauw and Christen, 2011) on ^{210}Pb -derived chronology and ^{14}C conventional ages and applying the ΔR values determined above (Fig. 3 and Table 2). The model is based on Bayesian statistics and determines the accumulation rate for each interval or section using several Markov Chain Monte Carlo (MCMC) iterations. This approach allows us to better constrain the uncertainties in the development of the age-depth model (Trachsel and Telford, 2017).

Table 2

^{14}C dates of modern pre-bomb samples in SD-6-MC and their reservoir ages (ΔR) with their standard deviation of the 95% confidence ranges calculated from their $^{210}\text{Pb}_{\text{xs}}$ derived calendar ages using the *Deltar* application (Reimer and Reimer, 2017). Abbreviations: bulk-OM: bulk organic matter; Plk. Foram.: mixed planktonic foraminifera.

Sample name	Composite depth (cm)	$^{210}\text{Pb}_{\text{xs}}$ age (Year CE)	Conventional radiocarbon age (BP)	ΔR (years)
ST6-SD-MC-10	15.4	1942 ± 8	1170 ± 20	706 ± 42
SD6-MC2-15.5	21.7	1909 ± 12	660 ± 15 (Plk. Foram.)	206 ± 32

According to the age model obtained, the sediment composite record covers the past 3500 years with an accumulation rate ranging between 0.03 and 0.3 cm.yr $^{-1}$ and a mean value of 0.08 cm.yr $^{-1}$ (Fig. 3).

To explore the significance of the chosen ΔR values on the resulting age model, models using our new ΔR values were compared to previous sediment chronologies from Soledad Basin (van Geen et al., 2003; Abella-Gutiérrez and Herguera, 2016; O'Mara et al., 2019; Abella-Gutiérrez et al., 2020).

4.4. Age-depth model offset

The ^{210}Pb derived chronology, radiocarbon ages, and depths were used to build the age model of the composite core RR18-SOL-MC1/SD6-MC/SD-6-GC2. To test the accuracy of age models obtained with different ΔR values, we generated age-depth models based on each ΔR value reported so far (Fig. 4). An age offset was estimated from the difference between the modeled mean age (years BP) achieved using our ΔR value, minus the resulting modeled mean age (years BP) applying the ΔR values used previously in this region. Likewise ^{14}C AMS dates made on sediment OM were also included in the age model, based on the established constant difference between them and carbonates (see section 4.2 of this study and Mollenhauer et al., 2003; 2005; Ausín et al., 2019), by adding a 500 years correction to the OM values.

The Bacon output age-depth models depicted in Fig. 4 show considerable differences when different ΔR values are applied. Small discrepancies are observed at the top (younger part) of the record. However, depending on the choice of ΔR value, the age offset varies with depth in the core (offset varies between -80 and 220 years). The greatest differences were observed when a ΔR value of 350 ± 50 years (Fig. 4b) was used: in this scenario, at 50 cm there is already an age offset of 100 years that remains constant until 250 cm where it reaches a maximum offset of 218 years. Additionally, the uncertainty involved in the Marine Reservoir Effect (MRE) also affects the age model: the age offset is constant around 50 years when applying a $\Delta R = 250 \pm 50$ years (Fig. 4a), whereas it becomes highly variable using a $\Delta R = 253 \pm 122$ years (Fig. 4c). The same is true for $\Delta R = 200 \pm 100$ years (Fig. 4d). Even though this value is similar to the MRE determined in this study (i.e., $\Delta R = 206 \pm 32$ years), the former displays age offsets oscillating around -100 to 100 years. These results highlight the impact not only of the ΔR values but also the uncertainty applied, and how these choices affect the sediment age-depth model (although the ΔR values presented in this study in comparison with the one presented by van Geen et al. (2003) are similar, the difference in the uncertainties appears to generate an evident offset). In a decadal context and with a short record (~ 2000 years), an inaccurate ΔR value and its uncertainty can lead to erroneous interpretations when comparing climatic time series from instrumental data (absolute ages) with reconstructed proxy records from sediments (model ages).

The MRE presented in this study was analytically assessed by complementing the radiocarbon model with an alternative dating method (^{210}Pb), whereas MRE estimates used in previous studies were determined more empirically. For instance, the $\Delta R = 350 \pm 50$ years value used by Abella-Gutiérrez et al. (2020) was devised to accommodate a ^{210}Pb chronology to the radiocarbon ages, by adding 100 years to the reservoir age for the area (a previous assessment of $\Delta R = 250 \pm 50$ years by Abella-Gutiérrez and Herguera, 2016), without pondering the consequences of undesirable age offsets in their climatic reconstructions (Fig. 4b). The MRE of 200 ± 100 years (van Geen et al., 2003, Fig. 4d) was determined by rounding to fewer significant figures and increasing the uncertainty of other published values (Stuiver and Braziunas, 1993; $\Delta R 225 \pm 25$ years; and Ingram and Souton, 1996; 233 ± 60 years), considering that there might be differences between the waters in which foraminifera and mollusks are calcifying (van Geen et al., 2003). Finally, in the scenario of Fig. 4c, the $\Delta R = 253 \pm 122$ years was calculated by using the weighted average of two nearby ΔR values (O'Mara et al., 2019), disregarding the nearest ΔR value (Fig. 1A; Magdalena Bay; 201

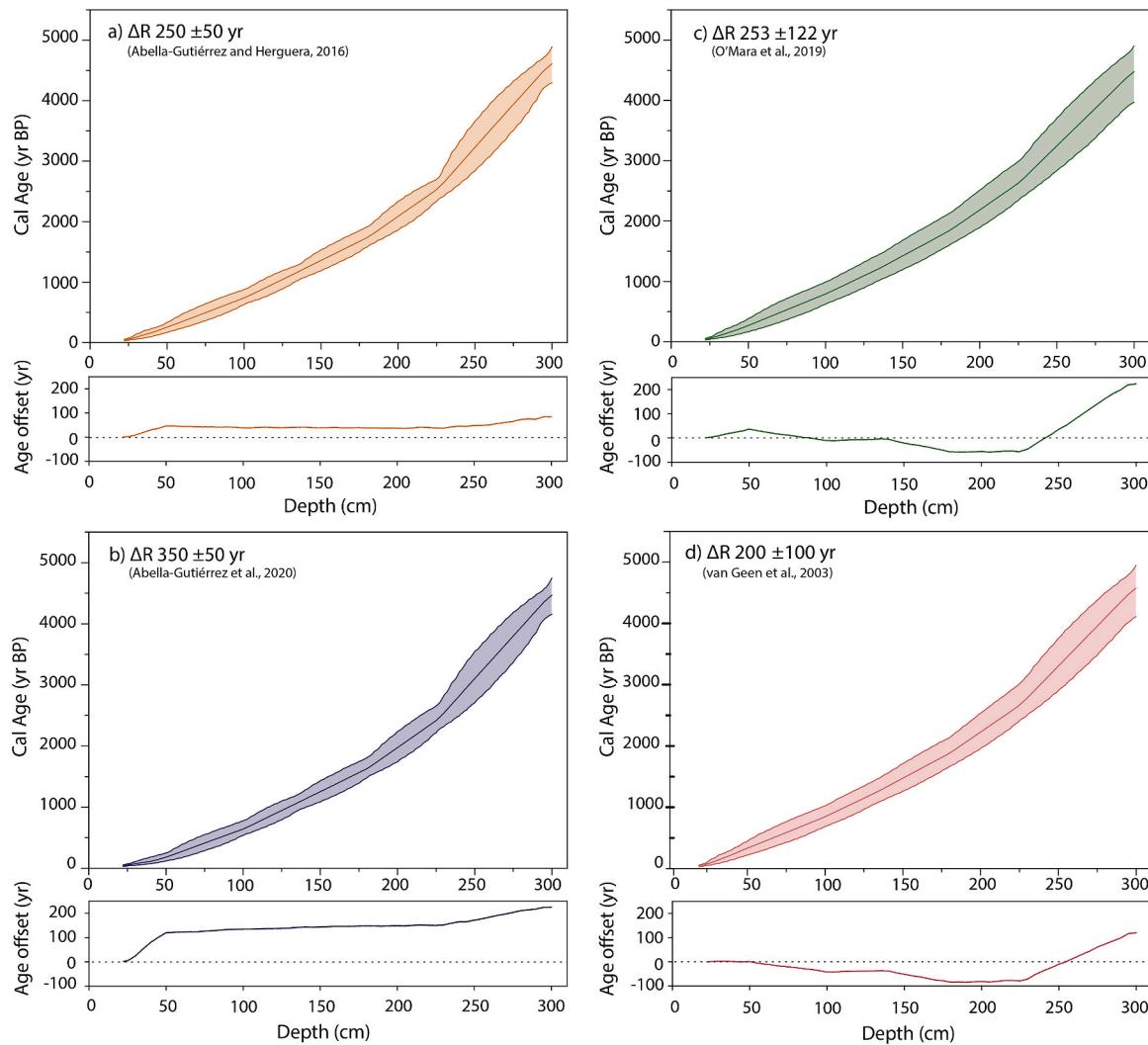


Fig. 4. Bacon output plots relating depth assignment to calendar years B.P. for composite core RR18-SOL-MC1/SD-6-MC/GC applying the different ΔR values published for Soledad Basin and reviewed in this study. The offset with respect to the age model established in this study is depicted below each graph (dotted horizontal line). The dashed line indicates the minimum and the maximum age (B. P.) estimated with Bacon software.

± 53 years) by claiming that mollusk shells at that site might have incorporated a non-trivial supply of terrigenous carbon from nearby mangroves, confounding radiocarbon measurements. It is pertinent to point out, however, that the ΔR value of Magdalena Bay was obtained from direct radiocarbon dating on *Anadara tuberculosa* (Berger et al., 1966; former *Arca tuberculosa*), a mollusk that lives buried in muddy sediments associated to mangroves roots (Félix-Pico et al., 2009). The fallibility of the assumption that its feeding habits might be integrating a signal different to the one expected for marine species was explained elsewhere: there are no significant differences between food habits and ecological niches in measured ^{14}C ages of mollusk shells across a variety of habitats (Ascough et al., 2005). The ΔR value calculated in the present study using an independent dating method is similar to the ΔR values assessed by Berger et al. (1966) for Magdalena Bay, confirming that this new ΔR is the most accurate for the Soledad Basin region, and consistent with the premise that the mollusk should have recorded a valid signal.

4.5. Palaeoceanographic implications

One of the multiple challenges in paleoceanography is to have a reliable age model to enable confident interpretations about the past. In addition to analytical considerations (e.g., careful ^{14}C protocols), assessment of accurate ΔR corrections is of high relevance. This is

especially true when working at decadal to multidecadal timescales. In this regard, recent studies in Soledad Basin have concluded that the Pacific Decadal Oscillation (PDO) is an important driver of multidecadal variability of sea surface temperature (O'Mara et al., 2019) and marine productivity (Abella-Gutiérrez and Herguera, 2016; Abella-Gutiérrez et al., 2020). Since PDO is apparently responsible for marking the tempo of productivity and SST variability in this region, we carried out a correlation analysis between the PDO index (MacDonald and Case, 2005) and our marine primary productivity proxy (TOC) to test the statistical significance of the different ΔR values used in Soledad Basin. For this, both series were resampled to a resolution of two years and a lowpass filter equivalent to 20 years was subsequently applied (Fig. 5a). Moreover, since the time series presented here did not fulfill the main assumptions of parametric statistics, a Spearman correlation was performed between the TOC and PDO data. An identical correlation was performed for each of the four age models obtained using the different ΔR values from prior reports and this work (Fig. 5b). This approach was carried out only to test the accuracy of the reconstructed chronologies generated by the different ΔR values with respect to the timing of PDO; it is out of the scope of this study to discuss the mechanisms and palaeoceanographic implications of the relationship between PDO and TOC, which will be the subject of a future paper (in progress). Our approach reveals there is a significant positive correlation between TOC

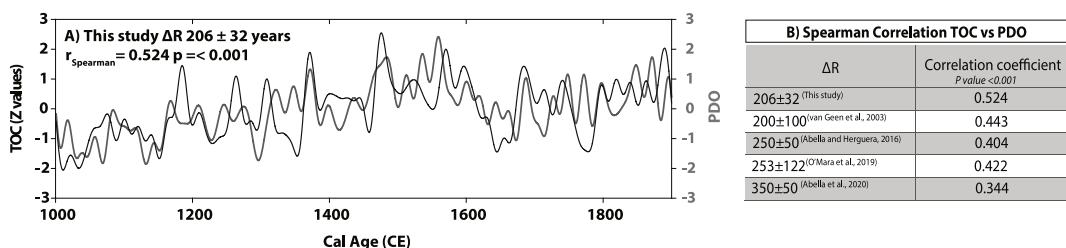


Fig. 5. Comparison between Total Organic Carbon (black line) and Pacific Decadal Oscillation (grey line; index from MacDonald and Case, 2005). Both series were filtered with a lowpass filter of 20 years. A) TOC versus PDO using the ΔR from this study; B) Table showing the coefficient correlation between TOC and PDO for each ΔR reviewed in this article. All correlations were statistically significant (p value < 0.001).

and PDO (0.524 $p < 0.001$). Although all correlations produced statistically significant values, our new assessment of the ΔR value for Soledad Basin produced the highest correlation with PDO (Fig. 5b).

Even though the ΔR value estimated here is used as a constant during the last 2000 years, it is essential to be aware that the MRE in an upwelling zone is not time-independent, and thus there might be some variability during late Holocene (Carré et al., 2016; Kennett et al., 1997; Ortílieb et al., 2011). Considering the age limit of the ^{210}Pb method, a different approach, as the application of the long-lived radionuclide ^{230}Th ($T_{1/2} = 75,380$ years; Geibert et al., 2019) should be used to confirm or offer a more suitable ΔR value for periods longer than the Holocene (i.e., deglaciation-glaciation), when significant changes in reservoir age took place (Lindsay et al., 2015).

5. Conclusion

A robust marine sediment core chronology requires proper estimation of the regional reservoir age correction (ΔR). In this study, we used the Paired Radiocarbon/Alternative Dating method by comparing the radiocarbon ages with the chronologies established with the $^{210}\text{Pb}_{\text{xs}}$ method to effectively estimate the local MRE correction for dating Late Holocene sediments in Soledad Basin. This approach allowed us to estimate a ΔR value of 206 ± 32 years for foraminiferal samples, and to assess the first ΔR value for the OM fraction in this region, which shows a constant age offset of ~ 500 years relative to the dates derived from foraminifera samples (i.e., $\Delta R_{\text{OM}} = 706$ years). When compared to the literature, the local MRE estimated in this study is similar to the first referenced value for this region, which was then disregarded by more recently published palaeoceanographic studies. Additionally, when testing the different ΔR values previously used in Soledad Basin against our estimated radiocarbon ages, we show that the age-depth models of the former display age offsets of up to 218 years for chronological reconstructions, which significantly impacts interpretation of climate proxy records. Correlation analysis shows that the chronology obtained with our ΔR assessment is the one that correlates most robustly with the timing of PDO.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.quageo.2021.101178>.

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