

## USING STABLE CARBON ISOTOPES TO QUANTIFY RADIOCARBON RESERVOIR AGE OFFSETS IN THE COASTAL BLACK SEA

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**ABSTRACT.** Constraining radiocarbon ( $^{14}\text{C}$ ) reservoir age offsets is critical to deriving accurate calendar-age chronologies from  $^{14}\text{C}$  dating of materials which did not draw carbon directly from the atmosphere. The application of  $^{14}\text{C}$  dating to such materials is severely limited in hydrologically sensitive environments like the Black Sea because of the difficulty to quantify reservoir age offsets, which can vary quickly and significantly through time, due to the dynamics of the biogeochemical cycling of carbon. Here we reconstruct  $^{14}\text{C}$  reservoir age offsets ( $R_{\text{shell-atm}}$ ) of Holocene bivalve shells from the coastal Black Sea relatively to their contemporaneous atmosphere. We show that the  $^{14}\text{C}$  reservoir age offset and the stable carbon isotope composition of bivalve shells are linearly correlated in this region. From a biogeochemical standpoint, this suggests that inorganic stable carbon isotope and  $^{14}\text{C}$  compositions of Black Sea coastal waters are controlled by the balance between autochthonous primary productivity and heterotrophic respiration of allochthonous pre-aged terrestrial organic matter supplied by rivers. This provided an important implication for Black Sea geochronology as the reservoir age offset of  $^{14}\text{C}$ -dated bivalve shell can be inferred from its stable carbon isotope composition. Our results provide a fundamental and inexpensive geochemical tool which will considerably improve the accuracy of Holocene calendar age chronologies in the Black Sea.

**KEYWORDS:** Black Sea, carbon cycle, reservoir age, freshwater reservoir effect, geochronology.

### INTRODUCTION

The radiocarbon ( $^{14}\text{C}$ ) reservoir age offset ( $R$ ) of an organism is the difference between its  $^{14}\text{C}$  age and that of the atmospheric  $\text{CO}_2$  at the time this organism was alive (Stuiver and Polach 1977; Ascough et al. 2005; Jull et al. 2013; Soulet et al. 2016).  $^{14}\text{C}$  reservoir age offsets are in  $^{14}\text{C}$  years. Very importantly, any  $^{14}\text{C}$  age obtained from an organism that did not incorporate its carbon directly from the atmosphere must be corrected for a reservoir age offset to provide an accurate estimate of its calendar age using the atmospheric  $^{14}\text{C}$  calibration curve (Reimer et al. 2013). These corrections are crucial as they can range from a few hundred to thousands of  $^{14}\text{C}$  years (Siani et al. 2000, 2001; Bondevik et al. 2006; Kuzmin et al. 2007; Soulet et al. 2011a).

Recent studies suggested that some geochemical characteristics of an organism could be related to its reservoir age offset. For instance, it has been shown that the  $^{14}\text{C}$  reservoir age offset of modern Baltic Sea *Macoma* bivalve shell was inversely related to its shell  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (Lougheed et al. 2016). Accurately determining the calendar age of  $^{14}\text{C}$ -dated archeological remains of human populations that draw their carbon from various sources as a result of mixed diet is challenging. For example, individuals from a population that mostly eats fish can have their stable carbon and nitrogen compositions impacted (Schoeninger et al. 1983; Schoeninger and Deniro 1984) and even exhibit a reservoir age offset (Dewar and Pfeiffer 2010; Olsen et al. 2010; Ascough et al. 2012; Wood et al. 2013). It has been shown from two archeological sites from the region of Lake Baikal that the  $^{14}\text{C}$  reservoir age offset of human bones was linearly correlated to their nitrogen isotopic composition ( $\delta^{15}\text{N}$ ) (Schulting et al. 2014), and for one site to both their  $\delta^{15}\text{N}$  and stable carbon isotopic compositions ( $\delta^{13}\text{C}$ ) (Bronk Ramsey et al. 2014;

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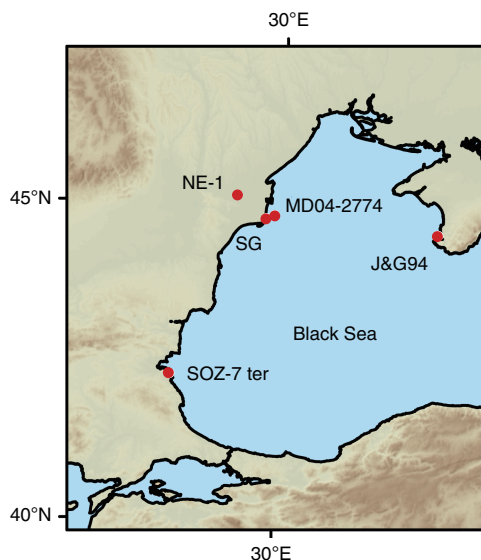


Figure 1 Western Black Sea area with sample locations and labels. (Coordinates are available in Supplementary material Table S1.)

Schulting et al. 2014). Another study showed that  $^{14}\text{C}$  reservoir age offset of human bones from a medieval Icelandic cemetery can be inferred using the nitrogen, carbon and sulfur isotopic compositions of the bones (Sayle et al. 2016). These studies are fundamental in the field of geochronology because they showed that it is possible to untangle the very complicated reservoir age offset correction issue.

The Black Sea is currently connected to the global oceans solely via the narrow and shallow Bosphorus Strait (Figure 1), leading to restricted water exchanges with the Mediterranean Sea and permanent stratification (Özsoy and Ünlüata 1997). During the last glacial lowstand and for much of the deglacial sea-level rise, the Mediterranean connection was closed and the Black Sea was a large lake (e.g., Ross et al. 1970; Badertscher et al. 2011). The understanding of the glacial-deglacial hydrologic changes of the Black Sea has been recently refined (e.g., Major et al. 2006; Bahr et al. 2006; Kwiecien et al. 2009; Soulet et al. 2011a, 2013), as well as of its Holocene evolution (e.g., van der Meer et al. 2008; Giosan et al. 2012; Coolen et al. 2013). However, a robust chronological framework for the Holocene Black Sea is still lacking, thereby limiting interpretation and still precluding an understanding of the sequence of events that led to the reconnection of the Black Sea to the Mediterranean Sea that occurred sometime during the early Holocene (Ryan et al. 1997; Aksu et al. 2002; Major et al. 2006; Giosan et al. 2009; Soulet et al. 2011b; Yanko-Hombach et al. 2014). The uncertainty surrounding the timing of the reconnection—and by extension, the Black Sea chronological framework—is related to unconstrained  $^{14}\text{C}$  reservoir age offset correction. This weakness has long been recognized (Jones and Gagnon 1994; Kwiecien et al. 2008; Giosan et al. 2009; Soulet et al. 2011a) but it has never been fully solved.

Here, we reconstruct  $^{14}\text{C}$  reservoir age offsets of bivalve shells from the coastal Black Sea and relate them to their  $\delta^{13}\text{C}$  values, in an attempt to define  $^{14}\text{C}$  reservoir ages on the basis of the relationship, with the potential to considerably improve the chronological framework of the Black Sea sediment archives.

## METHODS AND SAMPLES

Reconstructions of  $^{14}\text{C}$  reservoir age offsets typically rely upon  $^{14}\text{C}$  determinations on terrestrial/marine (or lacustrine) pairs or multiple pairs (Ascough et al. 2005; Jull et al. 2013; Soulet 2015; Soulet et al. 2016). From cores collected in the western coastal Black Sea (Figure 1), five single pairs of articulated bivalve shells and pieces of terrestrially derived plant material were sampled from the same sediment layers in order to ensure contemporaneous deposition, and their  $^{14}\text{C}$  ages and stable carbon isotope values were determined.

### Radiocarbon and Stable Carbon Isotope Measurements

As a pre-cleaning, the bivalve shells were sonicated and rinsed in deionized water at least 10 times. Then the shell carbonate was converted into  $\text{CO}_2$  following National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility's standard phosphoric acid hydrolysis procedure (McNichol et al. 1994). The analyzed terrestrial plant materials were subjected to NOSAMS standard acid-base-acid pretreatment and converted to  $\text{CO}_2$  through the sealed tube combustion method (McNichol et al. 1994). The  $\text{CO}_2$  was then converted to graphite and analyzed for its  $^{14}\text{C}$  composition by accelerator mass spectrometry (AMS) at NOSAMS. Two shell samples and two terrestrial plant material samples were prepared and graphitized at Centre de Datation par le RadioCarbone (CDRC, Lyon, France) following procedures similar to those performed at NOSAMS and measured by AMS at the Laboratoire de Mesure du Radiocarbonate (LMC14-ARTEMIS, Saclay, France). Results are corrected for the  $^{13}\text{C}/^{12}\text{C}$  ratio as measured on the AMS (Santos et al. 2007) and are reported in Fm notation. Fm is identical to the  $A_{\text{SN}}/A_{\text{ON}}$  metric (Stuiver and Polach 1977), the  $^{14}\text{a}_\text{N}$  notation (Mook and van der Plicht 1999), and to the  $F^{14}\text{C}$  notation (Reimer et al. 2004). Corresponding conventional  $^{14}\text{C}$  ages ( $\rho$ ) reported in  $^{14}\text{C}$  years Before Present (AD 1950) were calculated according to:

$$\rho = -8033 \ln(\text{Fm}) \quad (1)$$

The stable carbon isotope compositions of the dated samples were obtained from a 10%-aliquot taken out of the produced  $\text{CO}_2$ , and measured using an Optima or VG Prism series II stable Isotope Ratio Mass Spectrometer (IRMS) at NOSAMS.  $^{13}\text{C}/^{12}\text{C}$  ratios are reported in the  $\delta^{13}\text{C}$  notation (‰ relative to Vienna Pee Dee Belemnite, or VPDB).

### Reservoir Age Offset Calculation

$^{14}\text{C}$  reservoir age offsets of the bivalve shells, relative to their contemporaneous atmosphere ( $R_{\text{shell-atm}}$ ), were calculated based on the  $^{14}\text{C}$  ages of the paired bivalve shell ( $\rho_{\text{shell}}$ ) and terrestrially-derived plant material ( $\rho_{\text{plant}}$ ) (e.g., Ascough et al. 2005; Jull et al. 2013; Soulet et al. 2016):

$$R_{\text{shell-atm}} = \rho_{\text{shell}} - \rho_{\text{plant}} \quad (2)$$

The  $^{14}\text{C}$  ages of the terrestrially derived plant material are assumed to correspond to the  $^{14}\text{C}$  age of the atmosphere at the time the bivalves were living. Five  $R_{\text{shell-atm}}$  values were calculated according to this method, based on the following paired samples of Black Sea shells and terrestrially-derived plant materials found co-located in the same sediment layer:

- i) A pair of an articulated juvenile *Dreissena sp.* bivalve and a sample of fragile foliar material, picked from a peat where the bivalve was found embedded and dated to 10,600–11,080 (95%) cal yr BP (core SG in the modern Danube delta). The bivalve, being a juvenile, was small and could have easily been transported onto the marsh surface where the peat was developing.

- ii) A pair of a *Monodacna caspia* bivalve (single valve) and a fragile piece of *Phragmites* reed dated to 9040–9420 (95%) cal yr BP (core MD04-2774; offshore the modern Danube delta).
- iii) Two paired samples of an articulated *Mytilus galloprovincialis* bivalve and charcoal from a ~15-cm-thick archeological layer recovered in several cores (SOZ-7 cores; Alepu lagoon, Bulgaria) (Flaux et al. 2016). The archeological site, dated to 5050–5300 (95%) cal yr BP (beginning of Early Bronze Age), was a pile-dwelling settlement recently discovered in the present Alepu lagoon (Flaux et al. 2016). The piles were 1 m long and 5–6 cm diameter and are made of oak. The bark was still in place showing that the wood was used directly after felling. The small diameter of the piles suggest that they were less than 40 years old at felling (Flaux et al. 2016). The piles indicate the beginning of the pile-dwelling occupation and were dated to  $4550 \pm 30$   $^{14}\text{C}$  yr BP. The charcoal pieces that we used to calculate the reservoir age offsets were found in the archeological layer of the site occupation that lasted less than 80 years (Flaux et al. 2016). The two charcoal samples used were dated to  $4525 \pm 30$  and  $4475 \pm 30$   $^{14}\text{C}$  yr BP. These  $^{14}\text{C}$  ages are not significantly different from those of the piles (Flaux et al. 2016). This suggests that the charcoals must originate from wood that lived during the occupation, and thus characterized by very little old wood effect, if any.
- iv) A pair of an articulated *Dreissena polymorpha* bivalve and a sample of small fragments of twigs dated to 4540–4820 (95%) cal yr BP (core NE-1 in the inner Danube delta).

One additional  $R_{\text{shell-atm}}$  value was obtained from the calendar age of a mussel (*Mytilus galloprovincialis*) collected alive in 1931 (offshore of west Crimea) (Jones and Gagnon 1994). In this case, the  $^{14}\text{C}$  composition of the atmosphere in 1931 was obtained from linear interpolation of the  $^{14}\text{C}$  calibration curve IntCal13 (Reimer et al. 2013), then the  $R_{\text{shell-atm}}$  value was calculated according to the above equations (substituting the subscript “plant” by “IntCal13”). The  $^{14}\text{C}$  reservoir age offset of two bivalve shells collected alive during the 19th century in the Black Sea are reported in Siani et al. (2000) but stable carbon isotopes were not published, and thus cannot be included in this study.

All  $^{14}\text{C}$  and reservoir age offset data are compiled in the supplementary material (Table S1).

## RESULTS AND DISCUSSION

Calculated  $R_{\text{shell-atm}}$  values ranged widely between 340 and 1100  $^{14}\text{C}$  years. This finding demonstrates that reservoir age offsets varied substantially in Black Sea coastal environments during the Holocene. The  $\delta^{13}\text{C}_{\text{shell}}$  values also ranged widely between  $-8$  to  $+1\%$  VPDB. We also found that the  $R_{\text{shell-atm}}$  values are linearly correlated to the  $\delta^{13}\text{C}_{\text{shell}}$  values ( $r^2 = 0.87$ ;  $p$ -value  $< 0.01$ ;  $n = 6$ ) (Figure 2):

$$R_{\text{shell-atm}} = 473(\pm 58) - 68(\pm 13) \times \delta^{13}\text{C}_{\text{shell}} \quad (3)$$

### Biogeochemical Significance of the $R_{\text{shell-atm}}-\delta^{13}\text{C}_{\text{shell}}$ Line

In order to understand the biogeochemical implications of the line, we explore the potential  $^{14}\text{C}$ - $^{13}\text{C}$  end-members of the coastal Black Sea. Here, we use the isotopic form of the reservoir age offset. This metric called the  $\delta^{14}\text{R}$  value (Soulet et al. 2016) is calculated based on the exact same  $^{14}\text{C}$  measurements used to calculate  $R_{\text{shell-atm}}$ :

$$\delta^{14}\text{R}_{\text{shell-atm}} = 1000 \left( \frac{F_{\text{mshell}}}{F_{\text{mplant}}} - 1 \right) \text{‰} \quad (4)$$

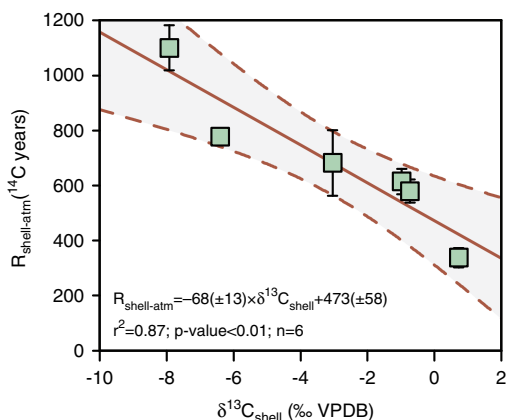


Figure 2 Linear regression of reservoir age offset ( $R_{\text{shell-atm}}$ ) and  $\delta^{13}\text{C}$  of Black Sea bivalve shells and its 95%-confidence interval.

The link between  $\delta^{14}\text{R}$  and  $R$  is straightforward:

$$R_{\text{shell-atm}} = -8033 \ln\left(\frac{F_{\text{mshell}}}{F_{\text{mplant}}}\right) \tag{5}$$

The  $\delta^{14}\text{R}$ - $\delta^{13}\text{C}$  relationship (Figure 3) is also a line ( $r^2 = 0.87$ ;  $p\text{-value} < 0.01$ ;  $n = 6$ ):

$$\delta^{14}R_{\text{shell-atm}} = -57.3(\pm 6.6) + 7.8(\pm 1.5) \times \delta^{13}C_{\text{shell}} \tag{6}$$

Over the observed range of  $\delta^{13}\text{C}$  values ( $-8$  to  $+1$  ‰ VPDB), the difference in the  $R_{\text{shell-atm}}$  inferred from Eq. 3 or Eq. 6 is minimal ( $< 10$   $^{14}\text{C}$  years). Instead, for very negative  $\delta^{13}\text{C}$  values the difference in calculated  $R_{\text{shell-atm}}$  can be up to thousands of  $^{14}\text{C}$  years. This is because  $R_{\text{shell-atm}}$  is a logarithmic function of the  $F_{\text{m}}$  values. This is why we must use the  $\delta^{14}\text{R}$ - $\delta^{13}\text{C}$  relationship to understand the biogeochemical processes explaining the line.

Bivalves form their carbonate shell primarily from the dissolved inorganic carbon (DIC) component of the water column, over several months to a few years as longevity of the bivalves studied here (*Mytilus galloprovincialis* and *Dreissena rostriformis*) is  $\sim 10$  years and probably less (Karatayev et al. 2006; Okaniwa et al. 2010). Thus, the shell isotopic composition reflects an integrated carbon isotopic composition of the DIC of the water in which they formed (Leng and Marshall 2004). The  $\delta^{14}R_{\text{shell-atm}}-\delta^{13}C_{\text{shell}}$  line (Eq. 6) indicates a  $^{13}\text{C}$  enrichment of the water DIC when the water DIC  $^{14}\text{C}$  composition becomes closer to that of the atmosphere (i.e.,  $\delta^{14}R_{\text{shell-atm}}$  becomes closer to 0‰). In other words, the  $^{14}\text{C}$  composition of the water DIC becomes equilibrated with that of the atmosphere, when its stable isotope composition becomes enriched in  $^{13}\text{C}$ . The enrichment in  $^{13}\text{C}$  may also result in DIC stable carbon isotope composition equilibration with that of the atmosphere but with a fractionation in  $\delta^{13}\text{C}$  from atmospheric  $\text{CO}_2$  to bicarbonate of 7 to 8‰ (Mook et al. 1974; Romanek et al. 1992).

The slope of the line suggests that the composition of the DIC of Black Sea coastal waters may have been driven mainly by the balance between autochthonous primary productivity and heterotrophic respiration of  $^{14}\text{C}$ -depleted (pre-aged) allochthonous terrestrial organic matter

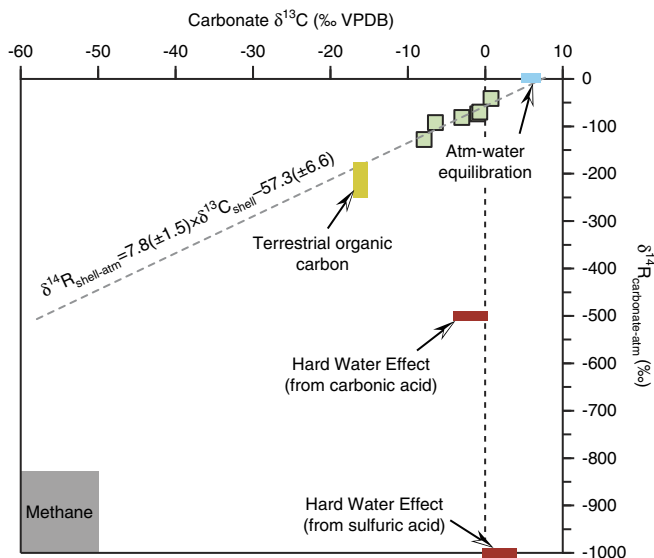


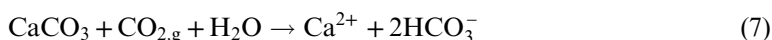
Figure 3 Linear regression of  $\delta^{14}R_{\text{shell-atm}}$  and  $\delta^{13}C$  of Black Sea bivalve shells (green squares;  $r^2=0.87$ ;  $p\text{-value} < 0.01$ ;  $n=6$ )—same samples as in Figure 2. Carbonate-equivalent endmembers of: i)  $CO_2$  atmosphere-water equilibration (blue rectangle), ii)  $CO_2$  from heterotrophic respiration of terrestrial organic matter supplied by rivers (yellow rectangle), iii) hard water effect from dissolution of outcropping carbonates by carbonic acid or sulfuric acid (red rectangles), and iv)  $CO_2$  from oxidation of methane (grey rectangle). Vertical dotted line is  $\delta^{13}C = 0\text{‰}$ . (See online version for colors.)

supplied by rivers. Indeed, the increased surface primary productivity during phytoplankton photosynthesis leads to  $^{13}C$  enrichment in the DIC (Hollander and McKenzie 1991; Leng and Marshall, 2004). This also leads to increased transfer of atmospheric  $CO_2$  to surface water via green algae and phytoplankton demand for  $CO_2$  (Deuser 1970; Hollander and McKenzie 1991; Li et al. 2017), and may result in an equilibration of the surface water  $^{14}C$  composition with that of the atmosphere, meaning that  $\delta^{14}R_{\text{shell-atm}}$  tends towards  $0\text{‰}$ . The latter is supported by  $^{14}C$  activity measurements of the DIC of Black Sea coastal waters in May 2004 showing that it had a similar  $^{14}C$  activity to that of the atmosphere on the day of sampling (Fontugne et al. 2009), with  $\delta^{14}R$  values of up to  $-4\text{‰}$  (equivalent to a reservoir age offset of only  $\sim 30$   $^{14}C$  years), i.e. very close to  $0\text{‰}$ . It is also supported by the presence of bomb  $^{14}C$  in short chain saturated fatty acids and alkenones—both produced by phytoplankton—extracted from core top sediments collected in the early 2000s from the coastal Black Sea (Kusch et al. 2010, 2016).

The primary productivity versus heterotrophic respiration balance hypothesis is further supported by the composition of the end-members defining the  $\delta^{14}R_{\text{shell-atm}}-\delta^{13}C_{\text{shell}}$  linear relationship. Indeed, assuming a complete productivity-driven equilibration of the surface water with the atmosphere, i.e.,  $\delta^{14}R_{\text{shell-atm}} = 0\text{‰}$ , the line predicts a  $\delta^{13}C_{\text{shell}}$  value of  $6.0 \pm 1.9\text{‰}$  VPDB for the carbonate phase (i.e., the mineral phase of the shell). At a range of temperatures typical for Black Sea surface waters, the  $\delta^{13}C$  of the carbonate phase is enriched by  $\sim 11\text{--}13\text{‰}$  compared to that of the  $CO_2$  phase (Romanek et al. 1992). Thus, the  $\delta^{13}C$  value of a carbonate derived from atmospheric  $CO_2$  with a pre-industrial  $\delta^{13}CO_2$  value of  $-6.4\text{‰}$  with respect to VPDB (Schmitt et al. 2012) would be of  $4.5$  to  $6.5\text{‰}$  VPDB. This range is in excellent agreement with the shell  $\delta^{13}C$  value of  $6.0 \pm 1.9\text{‰}$  VPDB, predicted by the line in the case of  $CO_2$  equilibration of the

surface water with the atmosphere (Figure 3). In addition, in the case of no autochthonous productivity at all, the organic matter utilized during heterotrophic respiration would have  $\delta^{13}\text{C}$  values of  $-25$  to  $-27\text{‰}$  VPDB, typical for Black Sea terrestrial organic matter (Kusch et al. 2010). Carbonate  $\delta^{13}\text{C}$  originating from pure respiration of terrestrial organic matter would thus range around  $-12$  to  $-16\text{‰}$  VPDB (Romanek et al. 1992), corresponding to predicted  $\delta^{14}\text{R}_{\text{shell-atm}}$  values of  $-150$  to  $-180\text{‰}$ . These latter values are compatible with surface sediment  $\delta^{14}\text{R}_{\text{sed-atm}}$  of  $-200\text{‰}$ , calculated from total organic carbon  $^{14}\text{C}$  ages offshore of the Danube River (Kusch et al. 2010) (Figure 3). Mineralization of pre-aged terrestrial organic matter by microbial respiration occurs in temperate lakes and streams of Quebec (McCallister and del Giorgio 2012). Our results suggest that pre-aged terrestrial organic matter as old as  $\sim 1500$   $^{14}\text{C}$  years supplied by rivers is also converted to  $\text{CO}_2$  by heterotrophic bacteria in the Black Sea coastal waters.

A hard water effect (HWE) origin, i.e., reservoir age offset mainly explained by the contribution of  $^{14}\text{C}$ -depleted riverine DIC from the dissolution of outcropping carbonates, seems unlikely. Indeed, carbonate minerals can be weathered through two main pathways. The carbonic acid pathway:



This pathway involves  $\text{CaCO}_3$  and atmospheric  $\text{CO}_2$  with  $\delta^{14}\text{R}$  values of  $-1000$  and  $0\text{‰}$  respectively, and  $\delta^{13}\text{C}$  values of  $\sim 0$  and  $-6.5\text{‰}$  VPDB (pre-industrial). Thus, the carbonate derived from the resulting DIC ( $\text{HCO}_3^-$ ) would have a  $\delta^{13}\text{C}$  value of  $-2$  to  $0\text{‰}$  VPDB (Romanek et al. 1992) and  $\delta^{14}\text{R}_{\text{HWE-atm}}$  of  $-500\text{‰}$  (Figure 3).

The second carbonate weathering pathway involves sulfuric acid, itself produced by the oxidation of sulfide minerals like pyrite (Calmels et al. 2007):



In this case the carbonate derived from the resulting DIC would have a  $\delta^{13}\text{C}$  value of  $\sim 0\text{‰}$  VPDB and  $\delta^{14}\text{R}_{\text{HWE-atm}}$  would be of  $-1000\text{‰}$ . None of these endmembers fits the coastal Black Sea  $\delta^{14}\text{R}$ - $\delta^{13}\text{C}$  line (Figure 3).

Oxidation of old methane could be another explanation, as it seems to impact the  $^{14}\text{C}$  composition of DIC of the present day Black Sea waters in the deeper part of the basin (slope and deep basin) (Fontugne et al. 2009). However, for very negative  $\delta^{13}\text{C}$  values typical of methane oxidation (e.g.  $-60\text{‰}$ ; Kessler et al. 2006), the extension of the line predicts a  $\delta^{14}\text{R}_{\text{shell-atm}}$  of  $-400$  to  $-450\text{‰}$ , in disagreement with  $\delta^{14}\text{R}$  values for Black Sea methane being as low as  $-850\text{‰}$  (Kessler et al. 2006). Thus, oxidation of methane is unlikely to explain the reservoir age offset in the coastal settings of the western Black Sea.

### Improving Black Sea Geochronology

The coastal Black Sea  $\text{R}_{\text{shell-atm}}\text{-}\delta^{13}\text{C}_{\text{shell}}$  line (Eq. 3; Figure 2) has fundamental implications for the Black Sea geochronology. It is now possible to use bivalve shell  $\delta^{13}\text{C}$  values as a proxy for reconstructing the reservoir age offset in the coastal Black Sea. Moreover, this  $\delta^{13}\text{C}$ -based tool can be applied on the same bivalve shell that is being  $^{14}\text{C}$  dated, leading to a customized reservoir age offset correction, which is crucial to providing an accurate estimate of the calendar age for the  $^{14}\text{C}$ -dated shell. Using this proxy is inexpensive since most  $^{14}\text{C}$  laboratories can provide the  $\delta^{13}\text{C}$  values of the dated material. One should note that the  $\delta^{13}\text{C}$  determination must be performed by IRMS on the  $\text{CO}_2$  produced from the dated material and reported vs. VPDB. The  $\delta^{13}\text{C}$  value measured on the AMS during  $^{14}\text{C}$  measurement should not be used because of potential large instrumental fractionation effects (Santos et al. 2007).

At this stage of the research, i) any vital effect on the  $\delta^{13}\text{C}$  value seems of second order importance, but the use of the  $R_{\text{shell-atm}}\text{-}\delta^{13}\text{C}_{\text{shell}}$  line should be restricted to bivalve shells and for  $\delta^{13}\text{C}$  values of 2 to  $-10\%$ ; ii) the application of the line should be restricted to the Holocene, in coastal to near coastal settings of the western Black Sea; iii) the line applies for both marine and lacustrine periods of the basin evolution—suggesting that the composition of the end-members did not change much through the Holocene and that the pathway of terrestrial carbon mineralization (from Black Sea lacustrine or marine biotic communities) is also of second order importance.

## CONCLUSION

Our results provide new pieces of information about carbon cycling in the coastal Black Sea. They suggest that the balance between primary productivity and heterotrophic respiration of terrestrial carbon supplied by rivers is governing the carbon isotopic composition of the Black Sea coastal waters since early Holocene. As a consequence, they provide an invaluable  $\delta^{13}\text{C}$ -based tool to quantify reservoir age offset for the Holocene Black Sea coastal settings. This will undoubtedly help refine our understanding of the hotly debated last reconnection of the Black Sea and more generally provide constrained calendar age-depth models to the numerous studied sediment archives of the Black Sea. Other basins, e.g., the Caspian Sea, the Aral Sea or large lakes, may potentially yield such correlation between the  $^{14}\text{C}$  reservoir age offset and  $\delta^{13}\text{C}$  value of shells and deserve future investigation. This study, in line with other pioneering studies (Bronk Ramsey et al. 2014; Schulting et al. 2014; Loughheed et al. 2016), shows that correlations between the reservoir age offset and another geochemical parameter from the same material must be sought, with the aim of untangling the problem of reservoir age offset when deriving calendar age chronologies from non-atmospheric  $^{14}\text{C}$  measurements.

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## SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2018.61>

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