Research Networking Programmes

Short Visit Grant ☐ or Exchange Visit Grant ☒

Scientific Report

***Proposal Title**:* Dating and TIming of fluxes into and out of the MarinE CArbon Reservoir of the MeDiterranean Sea (TIMECARD)

Application Reference N°: 5103

Roberta Guerra, Alma Mater Studiorum – Università di Bologna

1) Purpose of the visit

The main purpose of the TIMECARD exchange project is to provide an exact dating and timing of fluxes into and out the marine carbon reservoir of the Mediterranean Sea with full integration of radio-isotopic dating and stratigraphic techniques. To this end the age of deep-sea sediments retrieved from the Mediterranean will be determined from carbonate shells from foraminifera and sediments using accelerator mass spectrometry (AMS) radiocarbon dating.

However, several factors can influence proxy signals during sedimentation and burial, particularly in in deep sediments where the sedimentation rate is very low. The apparent age of bulk carbonate in sediment may be influenced by the contribution of detrital (transported) carbonate to the sedimentary record introducing a potentially age bias towards older ^{14}C ages for a given sediment horizon.

The age model developed for the selected deep-sea cores will be based on ^{14}C AMS radiocarbon ages performed on monospecific samples of planktonic foraminifera (*Globigerinoides inflata* and *Globigerinoides ruber*, var. alba and rosea) from the size fraction >150 μm, in tandem with bulk sediment radiocarbon dates decoupling relative contributions of organic and inorganic matter.

The latter step of the TIMECARD exchange visit project will include full integration and intercalibration of ^{14}C and ^{210}Pb dates, when possible, synoptically with other geochemical proxies such as stable carbon isotopes ($\delta^{13}C$), and stratigraphic data.

2) Description of the work carried out during the visit

The VECTOR oceanographic cruise (TRANSMED) investigated different pelagic areas of the Mediterranean Sea. Sediment cores were mainly collected in the Mediterranean Sea including the western part of the Algero-Balearic basin and the Oran Rise, close to the Arboran Sea (cores V4B and V4C), and the Eastern Mediterranean Sea (core V7Cbis) during the TRANSMED cruise within the VECTOR project (Figure 1, Table 1). A full description of the study area can be found in Barsanti et al., 2011 [i].

Fig. 1. Sampling stations of sediments and foraminifera collected in the Western and Eastern Mediterranean Sea during the TRANSMED cruise. Geographical coordinate datum in WGS84. Red cycles represent samples analysed within the TIMECARD project.

Table 1. Results synthesis of multi-proxy geochemical data for sediment cores collected in the Mediterranean Sea ([i]; Langone, personal communication).
.

Core	Latitude	Longitude	Depth (m)	OC (%)	$d^{13}C$ (‰)	C/N	^{210}Pb inventory (Bq m^{-2})	Location
Western Mediterranean								
V4B	36°29′.996N	0°59′.477W	2650	0.58	-22.46	7.00	5158±300	Western Algero-Balearic Basin
V3C	40°35′.730N	5°17′.490E	2748	0.30	-22.10	5.08	3437±177	Sardino–Balearic basin
Eastern Mediterranean								
V7Cbis	36°26′.996N	18°25′.660E	3925	0.27	-19.87	6.89	1437±25	Ionian Sea

The sediment was dried at 50° C and disaggregated in 200 mL deionized water, before wet sieving into <150 mm and >150 mm size fractions using additional deionized water. Samples of 12–25 mg of well-preserved planktonic foraminifera were hand-picked from the >250 mm size fraction.
Conventional AMS radiocarbon analysis of carbonate samples, such as speleothem, foraminifera and corals, as well as bulk sediments, requires the extraction of about 1 mg of C (10 mg of $CaCO_3$). Most laboratories prepare samples by decomposition of carbonates with phosphoric acid in evacuated glass tubes [ii]. The formed CO_2 requires further cleaning and conversion into graphite, but the entire processing of carbonated samples to graphite targets is thus labour intensive and time consuming [iv, v].
We tested a new approach for a simplified acid decomposition of carbonates to obtain CO_2 for conversion into AMS graphite targets, then applied to foraminifer shells and bulk sediments from the West and East Mediterranean Sea [iii]. Preferably 10 mg $CaCO_3$ were weighted in 12 mL vials and closed with a screw cap containing a butyl septum (Exetainer® vials, Labco, UK). Air was removed from the vials with a He flow of 100 ml/min using a double-walled needle (Thermo, Germany) inserted through the septum. Then 1 mL analytical grade H_3PO_4 (85%) was added, and the samples were kept at 75°C for 30 – 60 min in a Carbonate Handling System IonPlus+ to ensure complete decomposition of carbonates, and the formed CO_2 was then flushed with a He flow at 100 mL/min within 2 min to the AGE system by means of the double walled needle (Thermo Fisher, Gasbench). Any water was is retained on a phosphorous pentaoxide trap (Merk Sicapent®), and the CO_2 is then absorbed on the zeolite trap (Supelco®, X13, -60 mesh, 200 mg) of the AGE system within 2 min. Finally the pure CO_2 is thermally released (500 °C for 2 hours) into a selected reactor of the AGE, where it is converted with hydrogen to graphite on 4.5 mg iron powder (Alfa Aesar®, reduced iron 99%, -325 mesh) in about 2 hours. The graphite was pressed into targets, which were analysed on the accelerator MICADAS at the CNA, along with standards and process blanks. Oxalic Acid II (NIST-SRM-4990C) was the primary standard used for all ^{14}C measurements.

3) Description of the main results obtained

The radiocarbon concentration of the carbonate samples are given in Table 2 and Table 3. Normally between 200 and 600 monospecific foraminifera of >250 μm diameter were used, corresponding to a sample size of ~9 to 15 mg, whereas sediment sample size was 40 mg in order to have the target $CaCO_3$ content of 10 mg required for the AMS MICADAS (Table 2).
The performance of new approach for a simplified acid decomposition of carbonates with the Carbonate Handling System IonPlus+ was assessed using radiocarbon-free samples as blanks (Reference Material for Contemporary Modern Carbon-14, NIST 4990c Oxalic Acid II) and IAEA standards C1–C2 (IAEA C1 Marble and IAEA-C2 Travertine) after dissolution and graphitization by the AGE as unknowns. The radiocarbon measurements of the reference carbonate materials (IAEA-C1 and IAEA C-2) are very well reproduced and in agreement with their consensus values (Table 2). A comparison of the results with the new setup with the new Carbonate Handling System IonPlus+ and the AGE system doesn't show any strong difference between 30 and 60 minutes acid decomposition time (Table 2). The time sample requirement for sample preparation with this new system is considerable reduced, when compared to conventional preparation of carbonates, where

the entire processing of carbonate samples to graphite targets is thus labour intensive and time consuming [iv, v]. The new carbonate method to determine the radiocarbon content of carbonates by acid decomposition with the Carbonate Handling System IonPlus+ is thus well applicable to small samples containing less of 10 mg $CaCO_3$, and is especially useful for carbonate tests of foraminifera, where not much material is generally available.
Sediments and foraminifera samples from the Mediterranean Sea (Figure 1) were pretreated similarly following a 30 minute dissolution time with the new system. The bulk carbonate fraction of sediments and monospecific foraminifera ages are presented in Table 3. Radiocarbon measurements are reported as percent Modern Carbon (pMC). Dates are reported as conventional ^{14}C age to obtain the reservoir-corrected age. Calibration of the radiocarbon dates was undertaken using the Marine09 radiocarbon calibration curves [vi].

Table 2. Repetitive preparation and ^{14}C measurements, normalized to oxalic acid II reference material, with results given percent modern carbon (pMC) for the Reference Quality Control Materials (IAEA-C1 and IAEA C-2) measured with the AMS MICADAS.

Sample label	Material	Nominal value ^{14}C (pMC)	Measured value ^{14}C (pMC)
IAEA-C1[a]	Marble	0.00±0.02	0.10±0.01
IAEA-C1[a]	Marble	0.00±0.02	0.14±0.01
IAEA-C1[a]	Marble	0.00±0.02	0.11±0.01
IAEA-C1[b]	Marble	0.00±0.02	0.14±0.01
IAEA-C1[b]	Marble	0.00±0.02	0.11±0.01
IAEA-C1[b]	Marble	0.00±0.02	0.14±0.01
IAEA-C2[a]	Travertine	41.14±0.03	41.14±0.19
IAEA-C2[a]	Travertine	41.14±0.03	41.10±0.19
IAEA-C2[a]	Travertine	41.14±0.03	41.06±0.19
IAEA-C2[b]	Travertine	41.14±0.03	41.44±0.19
IAEA-C2[b]	Travertine	41.14±0.03	41.51±0.20
Standard reference			
Ox-II	Oxalic Acid	134.1	134.43±0.52
Ox-II	Oxalic Acid	134.1	134.26±0.53
Ox-II	Oxalic Acid	134.1	133.52±0.52
Ox-II	Oxalic Acid	134.1	133.85±0.53
Ox-II	Oxalic Acid	134.1	133.90±0.54
Ox-II	Oxalic Acid	134.1	134.46±0.54

Note: sample dissolution with the Carbonate Handling System IonPlus+ : a) 30 minutes, b) 60 minutes

Table 3 lists the ^{14}C dating results for monospecific foraminifera samples and bulk sediment samples from the Mediterranean Sea. ^{14}C ages obtained on monospecific foraminifera from deep-sea sediments must be corrected for the difference in the ^{14}C composition between the atmosphere and the sea surface [vii]. Sea surface reservoir ages (ΔR) are crucial to establish a common chronological framework for marine paleoproxies, and for understanding ocean-continent climatic relationships. In modern ocean, radiocarbon ages of samples formed in the ocean, such as shells, fish, etc., are generally several hundred years older than their terrestrial counterparts. This apparent age difference is due to the large carbon reservoir of the oceans, but because of complexities in ocean circulation the actual correction varies with location. This regional difference from the average global marine reservoir correction is designated ΔR [ix]. As a first approximation, ΔR is assumed to be a constant for a given region and is calculated from the difference in ^{14}C years of known age marine samples and the marine model age for that calendar age. The Mediterranean Sea revealed a typical modern reservoir age (~ 400 yr) similar to that of the Atlantic Ocean, which is assumed it constant through time during most of the past 18,000 carbon-14 years [viii]; however ^{14}C reservoir ages within the Mediterranean Sea, are large and variable according to the 2009 marine calibration dataset [viii, ix]. In the Mediterranean Sea, the apparent ^{14}C age of bulk carbonate in sediments is older when compared to foraminifera ^{14}C ages (Table 3). Although foraminifera shells are well suited for ^{14}C dating because the measured age marks the true time death of the organism, ^{14}C dating of sediments via planktonic foraminifera may differ from those of other sediment fractions, and this apparent discrepancy can be attributed by reworking as demonstrated by Heier-Nielsen [x].

Table 3. Radiocarbon measures and ages of sediment components from the Mediterranean Sea.

Sample	Cored depth (cm)	pMC	^{14}C conventional age (yr BP)	^{14}C calibrated age
Reference materials				
Ox-II - Oxalic Acid		134.43±0.52		
		134.26±0.53		
		133.52±0.52		
Foraminifera				
V4B (*G. inflata*)	1 -1.5	105.66±0.42	-442±32	modern
V3C (*G. inflata*)	1 -1.5	88.11±0.36	1017±32	1290-1530 BC
V7C (*G. ruber*)	1 -1.5	92.69±0.37	610±32	1799-1949 BC
Sediment				
V4B	1 -1.5	50.27±0.22	5,525±35	nd
V3C	1 -1.5	71.85±0.3	2,665±34	nd
V7C	1 -1.5	66.9±0.29	3,229±34	nd

nd = not determined: post-nuclear sample.

$^{210}Pb_{xs}$ and ^{137}Cs vertical profiles and inventories indicated that bioturbation processes are the dominant processes responsible for sediment reworking in the sampled areas within the Mediterranean Sea (Table 1 and Table 4). In particular, in the Oran Rise area, Barsanti et al. [i] calculated the highest values of sediment mixing layers (13 cm) and bioturbation coefficients (0.187 $cm^2\ yr^{-1}$). This area corresponds to core sample V4B, for which foraminifera radiocarbon ages resulted post-nuclear testing. Conversely, the Ionian Sea showed the lowest bioturbation rates (V7C bis) (Table 4). In turn, the apparent age of bulk carbonate in the sediment may be influenced by the presence of redistributed sediment and/or detrital carbonate, both of which introduce a bias towards older ^{14}C ages. Therefore, the accuracy of direct dating of climatic proxy records, simply by ^{14}C analysis of the bulk carbonate individual sediment component, may be questionable in some instances.

The fraction of biogenic carbonate can be estimated as follows:

$$pMC_{bulk} = \left(pMC_{detrital} \cdot detrital\ \ fraction\right) + \left(pMC_{biogenic} \cdot biogenic\ \ fraction\right) \qquad (1)$$

As old detrital carbonate from continental rocks is older than 50,000 years, the following equation is obtained:

$$pMC_{bulk} = \left(pMC_{biogenic} \cdot biogenic\ \ fraction\right) \qquad (2)$$

$$biogenic\ \ fraction = \frac{pMC_{bulk}}{pMC_{biogenic}} \text{ and } \ detrital\ \ fraction = 1 - biogenic\ \ fraction \qquad (3)$$

where pMC_{bulk} and $pMC_{biogenic}$ are the percent modern carbon measured in bulk carbonated sediments and that measured in foraminifera, respectively (Table 3).

The fraction of detrital carbonate in bulk sediments from the Mediterranean Sea, along with calculated fluxes are reported in Table 4. The carbonate detrital fraction accounts for over 50% of carbonate in sediments, and this points to an influence of redistributed sediment and/or detrital carbonate, which in turn, could explain the older AMS ^{14}C dates obtained for bulk sediments (Table 3). Organic carbon (OC) burial, calculated from the sediment MAR and the organic carbon (OC) content of sediments (Table 1 and Table 4), is more intensive in the Western Algero-Balearic Basin and the Sardino–Balearic basin within the Mediterranean Sea. Conversely, despite their relative fractions, the carbonate biogenic component of sediment shows a less variable flux across the Mediterranean Sea (Table 4).

Table 4. Results synthesis of sediment cores collected in the Mediterranean Sea.

Core	Carbonate biogenic fraction	Carbonate detrital fraction	SML (cm)	D_b ($cm^{-2}\ yr^{-1}$)	MAR ($g\ m^{-2}\ yr^{-1}$)	OC burial ($mg\ m^{-2}\ d^{-1}$)	IC burial ($mg\ m^{-2}\ d^{-1}$)	Biogenic IC burial ($mg\ m^{-2}\ d^{-1}$)	Detritic IC burial ($mg\ m^{-2}\ d^{-1}$)
V4B	0.52	0.48	13	0.187	25.19	0.42	2.61	1.24	1.37
V3C	0.18	0.82	6	0.046	56.66	0.51	8.35	6.81	1.54
V7Cbis	0.28	0.72	2	0.006	13	0.1	1.9	1.37	0.53

Conclusions

Radiocarbon age offsets between foraminifera and bulk carbonate samples were investigated in sediment cores from the Mediterranean Sea. Within the surface mixed layer, foraminifera ages were consistently younger than those of bulk sediments at corresponding depths; a combination of biological reworking of the surface mixed layer, as well redistributed sediments and detrital ^{14}C inputs from continental rocks may be responsible for these differences. These age differences could have important implications for extrapolation of radiocarbon ages from different fractions to date palaeoceanographic records in the Mediterranean Sea. In addition, several studies show the local reservoir age has varied in time and space in the Mediterranean Sea, and this may have affected ^{14}C ages obtained in planktonic foraminifera obtained in deep sediments from the Mediterranean Sea. The influence of all these variations must be understood in order to establish chronological scales and tuning, and to date and correlate climatic events in deep sea cores from different locations in the Mediterranean Sea. Further research is needed in order to have: a) detailed information on local reservoir age as a function of water masses and circulation within the Mediterranean Sea, b) additional AMS ^{14}C dates on different monospecific foraminifera, and c) higher resolution sediment records coupled with other geochemical proxies including other dating isotopes, which could help constrain the tuning of chronological scales within the Mediterranean Sea.

References
[i] Barsanti M., Delbono I., Schirone A., Langone L., Miserocchi S., Salvi S., Delfanti R., 2011. Sediment reworking rates in deep sediments of the Mediterranean Sea. Science of the Total Environment 409, 2959–2970.
[ii] Santos, F. J., Gómez Martínez, I., Agulló García, L., 14C SIRI samples at CAN: Measurements at 200kV and 1000 kV. Nuclear Instruments and Methods in Physics Research B, http://dx.doi.org/10.1016/j.nimb.2015.03.058.
[iii] Wacker L., R.-H. Fülöp, I. Hajdas, M. Molnár, J. Rethemeyer, 2013. A novel approach to process carbonate samples for radiocarbon measurements with helium carrier gas. NIM B 294, 214–217.
[iv] I. Hajdas, G. Bonani, S.H. Zimmerman, M. Mendelson, S. Hemming, C-14 ages of ostracodes from pleistocene lake sediments of the western Great Basin, USA – results of progressive acid leaching, 2004. Radiocarbon 46, 189–200.
[v] M. Schleicher, P.M. Grootes, M.J. Nadeau, A. Schoon, 1998. The carbonate C-14 background and its components at the Leibniz AMS facility, Radiocarbon 40, 85–93.
[vi] Reimer P et a., 2013. INTCAL13 and MARINE13 radiocarbon age calibration curves 0–50,000 years cal BP. Radiocarbon 55, 1869-1887.
[vii] Bard, E., 1988. Correction of accelerator mass spectrometry 14C ages measured in planktonic foraminifera: Paleoceanographic implications. Paleoceanography 3, 635–645.
[viii] Siani G., Paterne M., Michel E., Supizio R., S., Sbrana A., Arnold M., Haddad G., 2001. Mediterrranean Sea Surface Radiocarbon Reservoir Age Changes Since the Last Glacial Maximum. Science 294, 1917-1920.
[ix] Stuiver, M., and Reimer, P. J., 1993, Extended 14C database and revised CALIB radiocarbon calibration program, Radiocarbon 35, 215-230.
[x] Heier-Nielsen, S., Conradsen, K., Heinemeier, J., Knudsen, K.L., Nielsen, H.L., Rud, N., Sveinbjornsdottir, A.E., 1995. Radiocarbon dating of shells and foraminifera from the Skagen Core, Denmark: evidence of reworking. Radiocarbon 37, 119 – 130.

6) *Future collaboration with host institution (if applicable)*

On day June 23rd, Prof. Rafael Garcia-Tenorio, vice-director of the CNA, organised a half-day discussion with the staff of the Laboratorio de Investigacion de Radiocarbono I & II, coordinated by Dr. Francisco Javier Santos Arevalo. The goal was to discuss the results obtained during the TIMECARD exchange visit project, and above all to set the basis to establish a network for the transfer/exchange of knowledge, methodologies, and samples among the Centro Nacional de Aceleradores (CNA) - Universidad de Sevilla (ES), the Alma Mater Studiorum –Università di Bologna (IT), and the Institute of Marine Sciences – National Research Council (CNR-ISMAR, IT). A further step will be the establishment of an Erasmus Plus agreement between the Universidad de Sevilla (ES) and the University of Bologna for staff/students exchange on common research topics explored during the TIMECARD project.

7) **Projected publications / articles resulting or to result from the grant *(ESF must be acknowledged in publications resulting from the grantee's work in relation with the grant)***

All participating institutions of the TIMECARD exchange visit project, the Alma Mater Studiorum – Università di Bologna (IT), the Universidad de Sevilla – CNA (ES) and the ISMAR-CNR (IT), intend to publish the results obtained within the TIMECARD by incorporating them into a wider publication on a highly detailed reconstruction of the timing and fluxes in the marine carbon reservoir of the Mediterranean sea.

8) **Other comments (if any)**

I thank very much the European Science Foundation (ESF) for funding this research project. A big thank to Prof. Rafael Garcia-Tenorio (CAN, Universidad de Sevilla) for supporting this project from the application step to the discussion of the results, and to Dr. Francisco Javier Santos for the time he dedicated me and all learning experiences and invaluable guidance over radiocarbon analysis and dating with AMS MICADAS during my stay at the CNA. Last but not least, I wish to thank Lidia Agulló García for the invaluable help and competence during the samples preparation steps prior to AMS ^{14}C measurements.