

A New Approach to Process Planktonic Foraminifera for Radiocarbon Measurements

Roberta Guerra^{a,b}, Francisco-Javier Santos Arévalo^c, Rafael García-Tenorio^{c,d}*

^aUniversity of Bologna, Department of Physics and Astronomy, Viale Berti Pichat 6/2, 40127 Bologna, Italy

^bUniversity of Bologna, Centro Interdipartimentale di Ricerca per le Scienze Ambientali, CIRSA, Via S. Alberto 163, 48123 Ravenna, Italy

^cCentro Nacional de Aceleradores (Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Junta de Andalucía), Thomas Alva Edison 7, 41092 Seville, Spain

^dUniversity of Seville, Department of Applied Physics, ETSA, Avenida Reina Mercedes 2, 41012 Sevilla, Spain

Abstract

Carbonate shells from foraminifera are often analyzed for radiocarbon to determine the age of deep-sea sediments or to assess radiocarbon reservoir ages. The Centro Nacional de Aceleradores (CNA) is equipped for the AMS radiocarbon analysis with a MICADAS (MINI CARbon DAting System), and a sample processing line including vial flushing, carbonate dissolution and transfer of the evolved CO₂ from the septum sealed tubes to the automated graphitization equipment (AGE). In this work, we have tested a fully-automated setup from sampling the released CO₂ from small carbonate samples (i.e. foraminifera shells) for radiocarbon analysis, where the formed CO₂ is later flushed by helium flow by means of a double-wall needle mounted from the tubes to the zeolite trap of the existing AGE-2. This carbonate dissociation line essentially replaces the elemental analyser normally used for the combustion of organic samples to further reduce the effort involved for sample preparation. The automated method yields in low sample blanks of about 50,000 years. Results of the processed reference materials (IAEA-C1 and IAEA-C2) are in agreement with their consensus values. Using this automated dissociation line we were able to date samples of monospecific foraminifera shells (~10 mg) of ~ 1000 radiocarbon years.

Introduction

AMS ¹⁴C dating measured on foraminifer shells provides an important means of age model development for proxy records from sediment cores when the reservoir age is known (Stuiver et al., 1998). In the marine environment, the reservoir age at a certain location and water depth is related to the ventilation age of the prevailing water mass [Stern and Lisiecki, 2013]. Yet several complications have been highlighted that may lead to significant uncertainties when attempting to interpret foraminiferal ¹⁴C ages. These include the effects of bioturbation within the upper sediment column, faunal assemblage variations through time, secondary calcification, downslope transport and variations in atmospheric $\Delta 14C$ (Peng and Broecker, 1984; Adkins and Boyle, 1997; Broecker et al., 2006).

Conventional AMS radiocarbon analysis of carbonate samples such as speleothems, foraminifera and corals, requires the extraction of about 1 mg C (ca. 10 mg CaCO₃). Most laboratories prepare samples by decomposition of carbonates by phosphoric acid in evacuated glass tubes, with the formed CO₂ requiring further cleaning and conversion to graphite, but the entire processing is labor intensive and time consuming. The enhancement of sample preparation throughput should be considered as a key issue for AMS ¹⁴C measurements. Automation is a solution for the effective preparation of the samples, and some laboratories have actually carried out automation for the several steps in sample preparation (e.g., Longworth et al., 2013; Wacker et al., 2010a). Significant advances in the graphitization and accelerator mass spectrometry (AMS) dating of small samples

* Corresponding author, e-mail: roberta.guerra@unibo.it

have been made in recent years (e.g. Santos et al. 2007; Delqué-Količ et al. 2013), but few studies have specifically targeted small carbonate samples for use in oceanographic research (Wacker et al., 2013a,b; Freeman et al., 2016).

A fully-automated system to handle carbonates using wet chemistry directly connected with an AGE system for sample combustion and graphitization was installed at the Centro Nacional de Aceleradores (CNA), Seville in 2015. Here, we tested this automated system for a rapid acid decomposition of foraminifer shells to obtain CO₂ for conversion into AMS graphite targets by AGE. Yet, we describe the potential effects of another potentially complicating mechanism, that of dating foraminiferal shells within the sedimentary bioturbated zone or mixed layer.

Materials and Methods

Sampling and processing

Sediment cores were mainly collected in the southern basin of Mediterranean Sea, including the western part of the Algero-Balearic basin close to the Arboran Sea (V4B), the southern-central part of the Balearic abyssal plain (V3C) and the central Ionian abyssal plain (V7Cbis), during the oceanographic cruise VECTOR (TRANSMED). Oceanographic and sedimentological conditions have been described previously in detail (Barsanti et al., 2011; Kovačević et al., 2012). The sediment was dried at 50°C and disaggregated in 200 mL deionized water before wet sieving into <150 µm and >250 µm fractions using additional deionized water. Aliquots of ~10-20 mg of well-preserved monospecific planktonic foraminifera (~200-600 individuals) were hand-picked from the >250 µm size fraction of washed sediment samples from the 1-1.5 cm sections of cores V4B, V3C and V7Cbis.

Experimental procedure

The schematic automated setup to process carbonated samples is shown in Fig. 1. Primary and secondary standards were used at the CNA to test for sample dissolution with phosphoric acid and graphitization by the AGE as unknowns. Oxalic Acid II (Reference Material for Contemporary Modern Carbon-14, NIST 4990c) was the primary standard used for all ¹⁴C measurements. Secondary Standards used in this study and their consensus pMC values were IAEA C-1 Marble, infinite age (0±0.002), and IAEA C-2 Travertine, 7135±5 yr (0.4114±0.0003) carbonate materials. Aliquots of ~10 mg of carbonaceous material 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 65ml/min using a double-walled needle (Thermo Fisher, Gasbench) inserted through the septum. Fast carbonate dissolution and a complete conversion to CO₂ was ensured by adding 1 mL analytical grade H₃PO₄ (85%) and heating the sample vials to 85°C in a Carbonate Handling System CHS, IONPLUS+ (ETH, Zurich, Switzerland). The formed CO₂ was then flushed with a He flow at 65 mL/min within 2 min to the AGE system by means of a commercial available auto-sampler syringe (PAL-GC, CTC, Switzerland) (Fig. 1). Any water was retained on a phosphorous pentoxide trap (Merk Sicapent®), and the CO₂ was then absorbed on the zeolite trap (Supelco®, X13, -60 mesh, 200 mg) of the AGE-2 system within 2 min. Finally the pure CO₂ was thermally released (500 °C for 2 hours) into a selected reactor of the AGE-2, 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.

All ¹⁴C measurements were accomplished on the graphitized samples using a MICADAS (MIni Carbon DAting System) developed by the ETH Zurich (Synal et al., 2007; Wacker et al., 2010b), which was installed at the at the CNA, Seville in 2012 (Santos Arévalo et al., 2015).

Radiocarbon dates are reported as conventional ¹⁴C age in ¹⁴C year before present (¹⁴C yr BP, present 1950) to obtain the reservoir-corrected age. The dates have been corrected for natural

isotopic fractionation by normalisation to $^{13}\text{C} = -25\text{‰}$ VPDB, and calibrated with the Marine13 radiocarbon calibration curves with associated ΔR (Reimer et al., 2013).

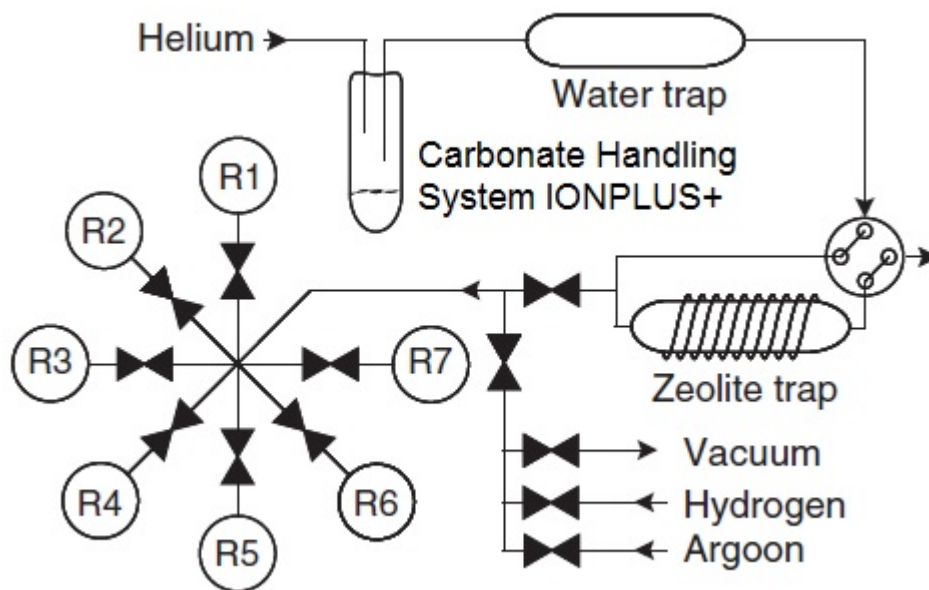


Figure 1. A schematic representation of the automated setup with the carbon dissociation line connected to the AGE with the zeolite trap and the 7 reactors (R1-R7)(modified from Wacker et al., 2010a).

Results and Discussion

A measurement procedure as usually performed at our MICADAS system for routine AMS measurements was applied with repeated analyses of samples, standards, and blanks to enable a statistical assessment of the dataset. During these measurements the overall ^{12}C transmission was 36-39%.

We used DBSP (Double Spar calcite) to quantify the contribution from the graphitization using the AGE-2 system and the automated carbonated dissolution line. Based on 3 experiments (30 and 60 minutes) with independent preparations and measurements, the mean blank pMC is 0.11 ± 0.01 , which translates to a ^{14}C age of $\sim 55,000$ years BP (Table 1). This shows that the combined system for sample dissolution and graphitization is able to reach old ages.

Based on six NIST 4990c Oxalic Acid II targets, the average pMC is 134.07 with a standard deviation of 0.01. These measured values agree with the standard value of 134.07 pMC (Table 1).

We also tested the influence of the time on carbonate decomposition (30 and 60 minutes) with phosphoric acid 85%. Radiocarbon measurements of processed reference carbonate materials (IAEA-C1 and IAEA-C2) are very well reproduced and in agreement with their consensus values (Table 1). The calculated means are 0.11 and 0.13 pMC (statistical spread: 0.01 and 0.02) for IAEA-C1 and 41.10 and 41.48 pMC (statistical spread: 0.04 and 0.05) for IAEA-C2, at 30 and 60 minutes decomposition time, respectively. A comparison of the results with the automated setup using the Carbonate Handling System IonPlus+ and the AGE-2 system showed that differences between the two treatments, tested by ANOVA, were highly significant for material IAEA-C2 ($p < 0.01$); post hoc comparison with SNK test showed significantly higher pMC values with a 60 minute dissolution time; conversely differences among the two treatments were not significant for reference material IAEA-C1.

Table 1. Repetitive preparation and radiocarbon measurement of reference carbonate materials normalized to oxalic acid II Reference material. Results are given in percent modern carbon (pMC) for the Reference Quality Control Materials IAEA-C1 and IEAEA-C2 measured with AMS MICADAS.

Sample label	Info	N analyses	Measured value ^{14}C (pMC)	Nominal value ^{14}C (pMC)
DBSP ^a		2	0.12±0.01	
DBSP ^b		2	0.11±0.01	blank
OX-II		6	134.07±0.37	134.07
IAEA-C1 ^a	Marble	3	0.11±0.01	0.00±0.02
IAEA-C1 ^b	Marble	3	0.13±0.02	0.00±0.02
IAEA-C2 ^a	Travertine	3	41.10±0.04	
IAEA-C2 ^b	Travertine	3	41.48±0.05	41.14±0.03

Dissolution time with 85% H_3PO_4 in the Carbonate Handling System CHS, IONPLUS+: a) 30 minutes, b) 60 minutes.

Monospecific planktonic foraminifera (*Globigerinoides inflata* and *Globigerinoides ruber*; size >250 μm diameter) from the deep Mediterranean Sea were pre-treated similarly following a 30 min dissolution time with the automated setup. This approach is less time consuming and requires a smaller amount of sample. However, it is necessary to convert radiocarbon age to calendar age because of the varying atmospheric ^{14}C content through time. For marine samples, this conversion requires an assumption about the ‘reservoir age’, or the offset in age between organisms that grow in the atmosphere and those that grow in a different carbon reservoir, such as the ocean (Stuiver et al., 1986). The Mediterranean Sea has a typical modern reservoir age (~ 400 yr), similar to that of the Atlantic Ocean in accordance with the modern oceanic circulation pattern, which is assumed to be constant through time during most of the past 18,000 carbon-14 years (Siani et al., 2001); however, larger variations in the Mediterranean ^{14}C reservoir ages have occurred in the past due to changes in the reservoir age of the North Atlantic water entering the Mediterranean Sea or fluctuations in continental runoff, which could introduce an additional source of uncertainty and potentially bias results by hundreds of years (Reimer and McCormac, 2002).

Table 2 lists the ^{14}C dating results of monospecific foraminifera samples from the Mediterranean Sea. Radiocarbon measurements are reported as percent Modern Carbon (pMC), and the dates are reported as conventional ^{14}C age to obtain the reservoir-corrected age. A ΔR value of 85 ± 1 years was used to correct for regional differences in the reservoir age within the Algero-Balearic basin and the Algero-Balearic abyssal plain, whereas a ΔR of 158 ± 40 was used for the Ionian Abyssal plain (Marine Reservoir correction Database; Reimer and Reimer, 2001).

Differences in radiocarbon age in the deep Mediterranean Sea (~2500 to ~4000 m depth) are recorded in planktonic foraminifers from the same depth interval between the Algero-Balearic basin and abyssal plain (core V4B and V3C), and the central Ionian abyssal plain (V7Cbis). Planktonic foraminifera from the Algero-Balearic basin (core V4B) with conventional negative radiocarbon ages (formed since mid 1950) cannot be calibrated, and highlighted an anomalous younger age probably reflecting the presence of bomb-produced atmospheric nuclear ^{14}C (Stuiver and Braziunas 1993; Reimer et al., 2004).

Although foraminifera shells are well suited for ^{14}C dating because the measured age marks the true time death of the organism, it is often difficult to distinguish between possible causes of observed

age anomalies as, e.g. downslope transport, secondary calcification, carbonate dissolution effects, or reworking in high-deposition rate deep-sea cores (Broecker et al., 1991, 2006).

Barsanti et al. (2011) indicated that bioturbation is the dominant processes responsible for sediment reworking in the deep areas of the Mediterranean Sea. The seafloor in the Algero-Balearic basin displayed a mixing depth of ~ 10 cm (SML) and a significant reworking activity (bioturbation coefficient, $D_b \sim 0.15 \text{ cm}^2 \text{ yr}^{-1}$). Conversely, the seafloor in the Balearic and the Ionian abyssal plains reported the lowest SML and D_b values ($\sim 2 - 6$ cm and $\sim 0.01 - 0.04 \text{ cm}^2 \text{ yr}^{-1}$, respectively). The age anomaly detected in the seafloor of Algero-Balearic basin may be explained by a combination of factors, i.e. downward mixing of foraminifera shells carrying the bomb- ^{14}C signature throughout the sediment mixed layer (SML). Conversely, the effect of bioturbation and related effects on our radiocarbon ages seems to be negligible in the Algero-Balearic and Ionian abyssal plains, and this is plausible considering the extremely high sedimentation rates recorded in these deep areas of the Mediterranean Sea (Zuniga et al., 2007; Garcia-Orellana et al., 2009). All evidence points to reworking of foraminifera and high sedimentation rates as the actual causes of the age discrepancies between the foraminifera from the same depth interval in sediments in the present case.

Table 2. Foraminifera samples were prepared with the automated method comprising acid decomposition under helium atmosphere using the Carbonate Handling System CHS, IONPLUS+. The graphite targets were measured together in one set with the same standards and blanks.

Sample label	Info/size	Measured value ^{14}C (pMC)	^{14}C conventional age (yr BP)	^{14}C calibrated age	$\delta^{13}\text{C}$ (‰)
V4B	<i>G. inflata</i>	105.66±0.42	-442±32	-	8.5
V3C	<i>G. inflata</i>	88.11±0.36	1017±32	1290-1530 BC	4.6
V7Cbis	<i>G. rubens</i>	92.69±0.37	610±32	1799-1949 BC	3.9

Conclusions

We are confident the new dedicated fully-automated line for carbonate samples will be far more accessible for radiocarbon analysis of users. It will put radiocarbon capabilities down to standard analytical techniques. Additionally, it has the advantage to target specific analysis of inorganic carbon from small carbonate samples only (i.e. foraminifera shells, speleotherms, corals, etc.), in contrast to the total carbon obtained when using an elemental analyzer. Quality assurance analyses of IAEA carbonate standards, which were processed by dissolution and graphitization, revealed good agreement between measured and consensus values.

Some radiocarbon age uncertainties remain due to reworking of foraminifer shells, as well as large and variable reservoir effects within the Mediterranean Sea. These age differences could have important implications for extrapolation of radiocarbon ages from different fractions to date palaeoceanographic records in deep sediments of the Mediterranean Sea. Future research will focus on: a) variations in regional reservoir ages as a function of water masses and circulation within the Mediterranean Sea, b) additional AMS ^{14}C dates on different monospecific foraminifera and other sedimentary components, and c) other geochemical proxies to constrain the tuning of chronological scales within the Mediterranean Sea.

References

Adkins, J. F., Boyle, E. A., 1997. Changing atmospheric D^{14}C and the record of deep water paleoventilation ages, *Paleoceanography* 12, 337- 344.

- 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. *Sci. Total. Environ.* 409, 2959-2970.
- Broecker, W.S., Klas, M., Clark, E., Bonani, G., Ivy, S., Wolfli, W., 1991. The influence of CaCO₃ dissolution on core top radiocarbon ages for deep-sea sediments. *Paleoceanography*, 6, 593-608.
- Broecker, W. S., Barker, S., Clark, E., Hajdas, I., Bonani, G., 2006. Anomalous radiocarbon ages for foraminifera shells, *Paleoceanography*, 21, PA2008, doi : 10.1029/2005PA001212.
- Delqué-Količ, E., Caffy, I., Comby-Zerbino, C., Dumoulin J-P, Hain, S., Massault, M., Moreau, C., Quiles, A., Setti, V., Souprayen, C., Tannau, J-F, Thellier, B., Vincent, J., 2013. Advances in handling small radiocarbon samples at the Laboratoire de Mesure du Carbone 14 in Saclay, France. *Radiocarbon* 55, 648-56.
- Freeman, E., Skinner, L.C., Reimer, R., Scrivner, A., Fallon, S., 2016 Graphitization of Small Carbonate Samples for Paleoceanographic Research at the Godwin Radiocarbon Laboratory, University of Cambridge. *Radiocarbon* 58, 89-97.
- Garcia-Orellana, J., Pates, J.M., Masqué, P., Bruach, J.M., Sanchez-Cabeza, J.A., et al., 2009. Distribution of artificial radionuclides in deep sediments of the western Mediterranean Sea. *Sci. Total Environ.* 407, 887-898.
- Kovačević, V., Manca, B.B., Ursella, L., Schroeder K., Cozzi, S., Burca, M., Mauri, E., Gerin, R., Notarstefano, G., Deponte, D., 2012. Water mass properties and dynamic conditions of the Eastern Mediterranean in June 2007. *Prog. Oceanogr.* 104, 59-79.
- Longworth, B.E., Robinson L.F., Roberts M.L., Beaupre S.R., Burke A., Jenkins W.J., 2013. Carbonate as sputter target material for rapid ¹⁴C AMS. *Nucl. Instrum. Methods Phys. Res. B* 294,328-334.
- Peng, T.H., Broecker, W.S., 1984, The impacts of bioturbation on the age difference between benthic and planktonic foraminifera in deep-sea sediments. *Nucl. Instrum. Methods Phys. Res. B* 233, 346-352.
- Reimer, P.J. Reimer, R.W., 2001. A marine reservoir correction database and on-line interface. *Radiocarbon* 43, 461-463.
- Reimer, P. et al., 2013. INTCAL13 and MARINE13 radiocarbon age calibration curves 0-50,000 years cal BP. *Radiocarbon* 55, 1869-1887.
- Reimer, P.J., McCormac, F.J., 2002. Marine radiocarbon reservoir corrections for the Mediterranean and Aegean Seas. *Radiocarbon* 44, 159-166.
- Reimer, P.J., Brown, T.A., Reimer, R.W., 2004. "Discussion: Reporting and Calibration of Post-Bomb¹⁴C Data", *Radiocarbon* 46, 1299-1304.
- Sanders, C.J., Santos, I.R., Silva-Filho, E.V., Patchineelam, S.R., 2006. Mercury flux to estuarine sediments, derived from Pb-210 and Cs-137 geochronologies (Guaratuba Bay, Brazil). *Mar. Pollut. Bull.* 52, 1085-1089.
- Santos Arévalo, F.J., Gómez Martínez, I., Agulló García, L., 2015. ¹⁴C SIRI samples at CNA: Measurements at 200 kV and 1000 kV. *Nucl. Instrum. Methods Phys. Res. B* 361, 322-326.
- Santos, G.M., Southon, J.R., Griffin, S., Beaupre, S.R., Druffel, E.R.M., 2007. Ultra small-mass AMS ¹⁴C sample preparation and analyses at KCCAMS/UCI Facility. *Nucl. Instrum. Methods Phys. Res. B* 259(1), 293-302.
- Siani, G., Paterne, M., Michel, E., Supizio, R., Sbrana, A., Arnold, M., Haddad, G., 2001. Mediterranean Sea Surface Radiocarbon Reservoir Age Changes Since the Last Glacial Maximum. *Science* 294, 1917-1920.
- Stern, J.V., Lisiecki, L.E., 2013. North Atlantic circulation and reservoir age changes over the past 41,000 years. *Geophys. Res. Lett.*, 40, 3693-3697.
- Stuiver, M., Pearson, G.W., Braziunas, T.F., 1986. Radiocarbon Age Calibration of Marine Samples Back to 9000 cal yr BP. *Radiocarbon* 28, 980-1021.
- Stuiver, M., Braziunas, T.F., 1993, Modeling atmospheric ¹⁴C influences and ¹⁴C ages of marine samples back to 10,000 BC, *Radiocarbon* 35:137-189.
- Stuiver, M., Reimer, P. J., Bard, E., Beck, J.W. G., Burr, S., Hughen, K.A., Kromer, B., McCormac, G., Van der Plicht, J., Spurk, M., 1998. INTCAL98 radiocarbon age calibration, 24,000 – 0 cal BP, *Radiocarbon*, 40, 1041-1083.
- Synal, H.A., Stocker, M., Suter, M., 2007. MICADAS: a new compact radiocarbon AMS system *Nucl. Instrum. Methods Phys. Res. B* 259, 7-13.
- Wacker, L., Nemeç, M., Bourquin, J., 2010a. A revolutionary graphitisation system: fully automated, compact and simple. *Nucl. Instrum. Methods Phys. Res. B* 268, 931-934.

- Wacker, L., Bonani, G., Friedrich, M., Hajdas, I., Kromer, B., Nemeč, M., Ruff, M., Suter, M., Synal, H.-A., Vockenhuber, C., 2010b. MICADAS: routine and high-precision radiocarbon dating, *Radiocarbon* 52, 252-262.
- Wacker, L., Fülöp, R.-H., Hajdas, I., Molnár, M., Rethemeyer, J., 2013a. A novel approach to process carbonate samples for radiocarbon measurements with helium carrier gas. *Nucl. Instrum. Methods Phys. Res. B* 294, 214-217.
- Wacker, L., Lippold, J., Molnár, M., Schulz, H., 2013b. Towards radiocarbon dating of single foraminifera with a gas ion source. *Nucl. Instrum. Methods Phys. Res. B* 294, 307-310.
- Zuniga, D., Garica-Orellana, J., Calafat, A., Price, N.B., Adatte, T., Sanchez-Vidal, A. et al., 2007. Late Holocene fine-grained sediments of the Balearic Abyssal Plain, Western Mediterranean Sea. *Mar. Geol.* 237, 25-36.

Acknowledgements

We are indebted to Ms Lidia Agulló García and Aurora Diéguez Ferrari for the assistance in the laboratory in sample preparation prior to AMS ^{14}C measurements. This project was supported by the European Science Foundation (ESF) Exchange Visit Grant 5103 'Dating and Timing of fluxes into and out of the Marine Carbon Reservoir of the Mediterranean Sea (TIMECARD)' awarded within the Research Networking Programme Earthtime – The European Contribution (EARTHTIME-EU). Special thanks to Leonardo Langone from the CNR-ISMAR for providing the planktonic foraminifera samples along with numerous geochemical proxies used to interpret data from this study.