RESEARCH AND DEVELOPMENT OF THE ARTEMIS ^{14}C AMS FACILITY: STATUS REPORT

C Moreau[1] • I Caffy • C Comby • E Delqué-Količ • J-P Dumoulin • S Hain • A Quiles • V Setti • C Souprayen • B Thellier • J Vincent

Laboratoire de Mesure du Carbone 14 (LMC14), UMS 2572, Bâtiment 450, porte 4E, CEA Saclay, 91191 Gif-sur-Yvette, France.

ABSTRACT. The Artemis accelerator mass spectrometry (AMS) facility is dedicated to high-precision radiocarbon measurements. It routinely measures over 4500 samples a year for French laboratories. This paper is a status report, showing the measurements of standard, blank, and FIRI intercomparison samples. Since 2008, research and development programs have been established by the Artemis team. During the collaborations with other research laboratories, intercomparisons on archaeological samples were performed and are listed here to show the quality of the Artemis measurements. Three areas of specific research and development are investigated: technical development, beam optic simulations, and specific archaeological studies. The technical developments of the facility are based on the setup of a new bench for water sample preparation and routine microsample preparation and measurement. Beam optic simulations are carried out to control the quality of the measurement related to the tuning of the facility. International collaborations are always in progress. In 2012, the programs include improving the accuracy of reigns for the dynastic Egypt period and the ^{14}C dating of ancient iron.

INTRODUCTION

The Artemis accelerator mass spectrometry (AMS) facility is located in Saclay, France, in the Laboratoire de Mesure du Carbone 14 (LMC14) AMS preparation and measurement laboratory. Artemis is based on a 9SDH-2 Pelletron tandem from National Electrostatic Corporation (NEC). The facility has been operating since 2003 and is fully devoted to radiocarbon dating. Over the years, the throughput has gradually increased, and since 2009, Artemis has routinely measured from 4500 to 4800 samples a year, which corresponds to ~3200 unknown samples, ~1400 samples to control the quality of the measurement (standards, blanks, and intercomparison samples), and more than 200 samples for specific research and development programs.

The Artemis facility is equipped with 2 MC-SNICS cesium sputter ion sources in order to minimize downtime. One source is a standard NEC 134-position source, and the other is a modified 40-position source provided by NEC in 2006. The routine running conditions for both sources were reported in a previous publication (Cottereau et al. 2007). An overview of the Artemis facility is presented on the Figure 1.

A 45° electrostatic spherical analyzer (ESA) selects the source and directs the beam to the 90° bending magnet. The 3 carbon isotopes are sent sequentially through the accelerator. The frequency of the bouncing system is 10 Hz. The low-energy negative currents $^{12}C^-$ and $^{13}C^-$ are measured during the cycle in an offset Faraday cup. The ratio of these 2 quantities can give an estimation of the number of CH molecules, by comparing this ratio with the standard isotopic ratio. The typical $^{12}C^-$ current expected for the 134-position ions source is about 40–50 μA, which is used for samples with a mass >0.2 mg of carbon. The 40-position ion source is devoted to the microsamples (<0.2 mg of carbon) and the $^{12}C^-$ current is limited during the tuning to 10–20 μA to avoid burning the sample too fast. The tandem accelerator is set up at 2.6 MV, and the stripping of ions is realized by collisions with argon gas in the stripper canal. The 3+ charge state is selected in the high-energy beam line. The overall transmission of the ^{12}C is ~50%. A 110° analysis magnet sends the ions into the rare isotope beam line. $^{12}C^{3+}$ and $^{13}C^{3+}$ currents are collected after the magnet in 2 independent offset Fara-

[1]Corresponding author. Email: Christophe-r.moreau@cea.fr.

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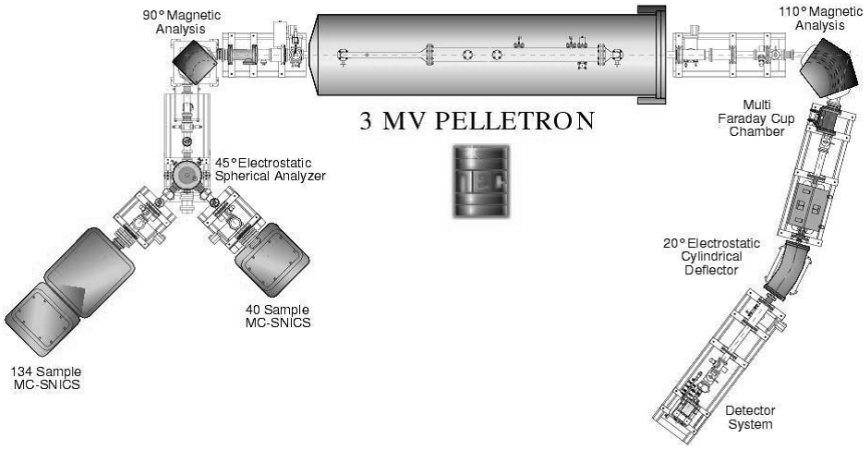

Figure 1 Artemis, the 3MV Pelletron AMS system

day cups, and they provide an on-line measurement of the $\delta^{13}C$, which is used to correct the ^{14}C ages. After focusing in a doublet quadrupole, $^{14}C^{3+}$ ions pass a 20° electrostatic cylindrical analyzer (ECA) and reach the ionization chamber that is filled with a mixture of argon (90%) and methane (10%) at a pressure of 63 Torr. At this time, the $^{14}C^{3+}$ ions are counted.

RESULTS

Normalization of all the measurements is done with the oxalic acid I (Ox-I) standard provided by IAEA (Rozanski et al. 1992). One standard per 10 unknown samples is put on the sample holder. ANU is used as a secondary standard and gives good results in agreement with the consensus values: 150.0 ± 0.5 pMC compared to the consensus value of 150.6 ± 0.1 pMC (Mook and van der Plicht 1999) (see Figure 2). This discrepancy is undesirable and oxalic acid II (Ox-II) may become the preferred secondary standard. A large volume of Ox-II will therefore be produced and tests will be performed to validate whether the Ox-II preparation is a suitable secondary standard.

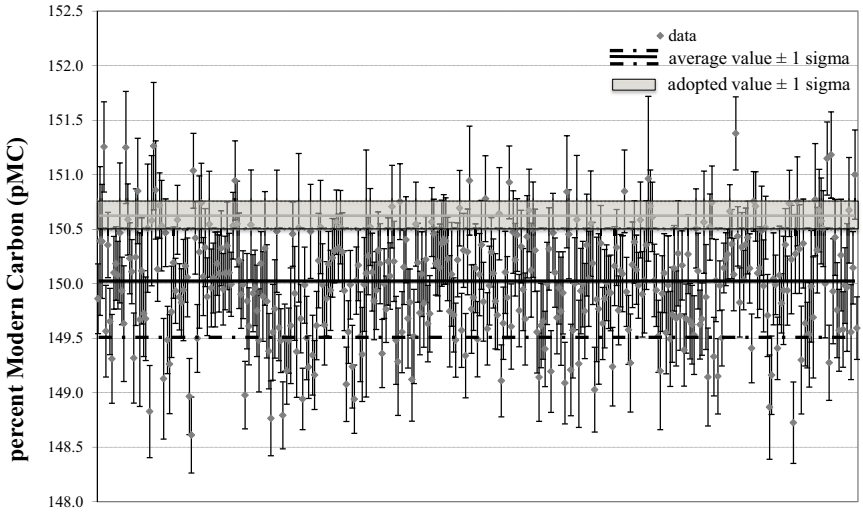

Figure 2 Result for ANU sucrose secondary standard (*x* axis in arbitrary units)

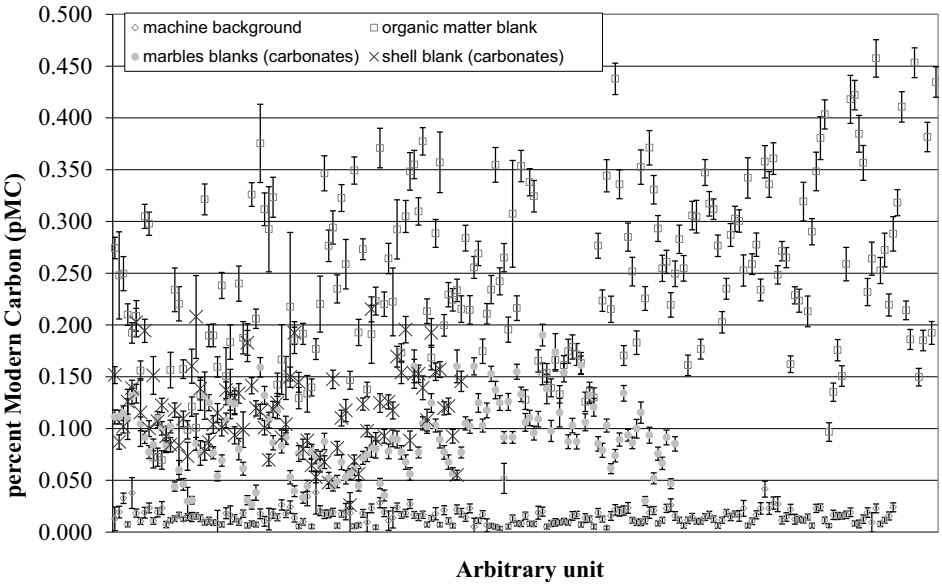

Figure 3 Evolution of unprocessed blank and processed blanks

The background of the machine is regularly checked with unprocessed blank graphite (Figure 3). The average value of the unprocessed blank is 0.015 ± 0.007 pMC, corresponding to an apparent age of 71,700 ± 4000 BP. Different processed blanks are used according to the nature of the processed samples, in order to control the ^{14}C contamination during different chemical treatments. Figure 2 shows the results for each kind of processed blank and Table 1 gives the statistical values for these blanks. Carbonate blanks are estimated by 2 kinds of processed blanks: C1 (IAEA) for marble and *Tridacna* shell for every kind of shell or foraminifera. The C1 average is about 0.091 ± 0.034 pMC, giving an age of 56,250 ± 3400 BP. *Tridacna* shell results average about 0.118 ± 0.040 pMC and the corresponding age is 54,150 ± 3000 BP. Charcoal blanks show higher values, with an average of 0.244 ± 0.084 pMC and an age of 48,300 ± 3000 BP. The variability is also higher due to the intrinsic variability of the piece of charcoal itself. All the processed blank values are much higher than the machine background.

Table 1 Values measured at Artemis for unprocessed and processed blanks.

Sample type	Nr of cathodes	Value measured at Artemis	
		pMC	Age BP
Charcoal	193	0.244 ± 0.084	48,300 ± 3000
Tridacna	82	0.118 ± 0.040	54,150 ± 3000
IAEA C1	132	0.091 ± 0.034	56,250 ± 3400
Ceylon[a]	183	0.015 ± 0.007	71,700 ± 4000

[a] With pretreatment.

Intercomparison samples are also used to check, in different time ranges, the accuracy of the Artemis measurements and, eventually, if a bias exists. Depending on the expected age of the unknown samples, FIRI C, E, G, H, I, and IAEA C2 (Scott 2003) are routinely used during measurements. The results are shown in Figure 4 for all FIRI and C2. Table 2 summarizes the average values.

Table 2 Average values for FIRI and C2. For FIRI C, E, H, and I values are given in ^{14}C yr before present (BP) and for FIRI G, C2 and ANU values are given in percent modern carbon (pMC).

Type	Nr of cathodes	Value measured at Artemis	Consensus value	Error multiplier
FIRI C[a]	51	18,358 ± 78 BP	18,176 ± 11 BP	1.2[b]
FIRI E	51	11,809 ± 54 BP	11,780 ± 7 BP	1.1
FIRI G	25	110.70 ± 0.35 pMC	110.70 ± 0.04 pMC	1.0
FIRI H	49	2238 ± 28 BP	2232 ± 5 BP	1.0
FIRI I	38	4498 ± 30 BP	4485 ± 5 BP	1.0
IAEA C2	59	41.12 ± 0.23 pMC	41.14 ± 0.03 pMC	1.1
ANU C6	383	150.00 ± 0.49 pMC	150.61 ± 0.11 pMC	1.3[b]

[a]With pretreatment.
[b]The mean value used instead of the adopted value in the calculation of the error multiplier.

Some failures of the graphitization process were observed on the LMC14 graphitization lines for FIRI C. Pollutants (chlorine) poison the reaction. In order to get 100% success in graphitization for these samples, a chemical pretreatment was added to the recommended chemical process for those samples. First, a leaching on carbon is done and then the sample is washed at pH = 7 with deionized water. Thus, the comparison with the consensus value is replaced with the average of our own measurements for FIRI C. In this case, some FIRI C samples, with recommended treatment, were graphitized with success and measured. The difference between with pretreatment and without pretreatment shows an offset of about 200 yr (Figure 4a). A statistical treatment is thus achieved to control the accuracy and the reproducibility of the FIRI C results. An error multiplier is calculated for each intercomparison sample (Scott 2003). The results are given in Table 2.

Table 2 reports all experimental data since the beginning of the year 2005, corresponding to the last change in the whole chain of production and measurement. All the individual error multiplier values are close to 1. This means that the experimental data are in perfect agreement (at 1σ) with the consensus value and shows that there is no bias in any range of ages tested with the intercomparison samples. In addition, the provided errors on each result are representative of the real error in the ^{14}C ages.

TECHNICAL DEVELOPMENTS AND SPECIFIC RESEARCH PROGRAM

The LMC14 team is fully involved in the development of the Artemis AMS facility. The 2 main areas of development are 1) technical optimization of the preparation process and ion beam optics studies; and 2) specific research programs in an archaeological context.

The technical development of the facility in 2012 was done to widen the range of sample types treated. It was based on the setup of a new bench for water sample preparation. A performance test was conducted in June 2012 (Dumoulin et al., these proceedings). The graphitization process has been also optimized for the ultra-small samples. The 2 routine graphitization benches are fully automatic. Each of them contains 12 reduction reactors of 18 and 12 mL. The evolution of the reduction yield with decreasing mass and the minimum mass that can be reduced with acceptable reproducibility has been studied under the routine conditions.

Several sets of microsamples produced from the normalizing standard Ox-I, international references, and blanks have been measured with optimized source setup to minimize the deterioration of the smallest targets under the cesium beam. The first measurements led to adjusting the amount of Fe catalyst for very small quantities of carbon to avoid the too-rapid destruction of the target under the beam. We observed that the $^{14}C/^{12}C$ ratio varied with the quantity of carbon present in the sample

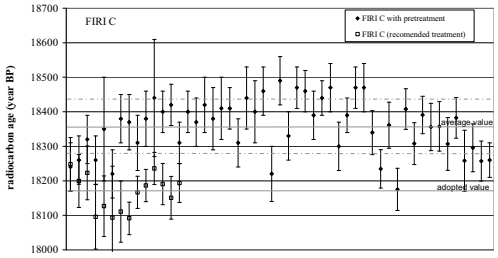

Fig 4a

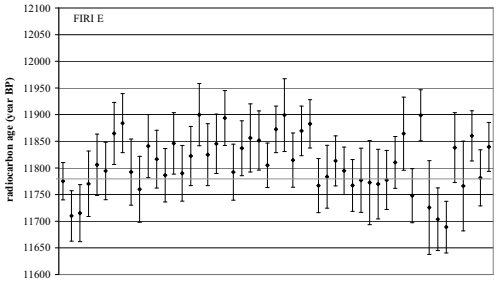

Fig 4b

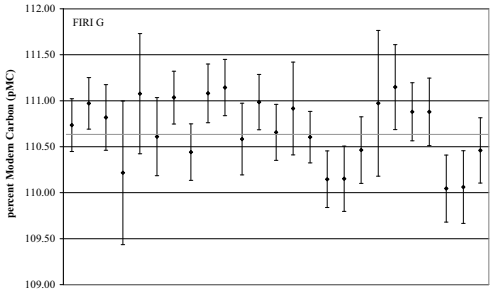

Fig 4c

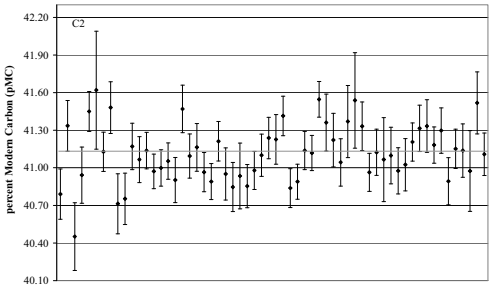

Fig 4d

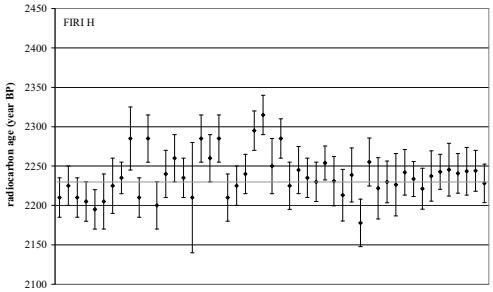

Fig 4e

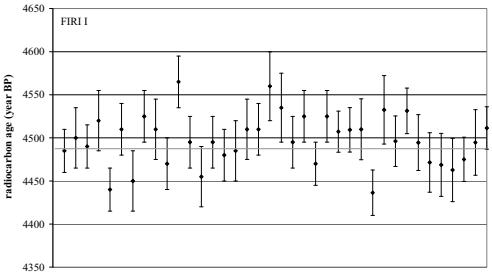

Fig 4f

Figure 4 Results for FIRI C (4a), FIRI E (4b), C2 (4c), FIRI I (4d), FIRIH (4e), and FIRI G (4f). The gray line indicates the adopted value for each kind of intercalibration sample. *X* axes are in arbitrary units.

and with the $^{12}C^{3+}$ beam current intensity. The quantification of the modern and dead contamination in the graphitization process is under study to increase the graphitization yield and reduce the effect of contamination. A smaller reactor volume is thus used. The carbon extraction process—combustion for organic matter and hydrolysis for carbonates—is also considered in terms of modern carbon contamination. As expected, the contamination is slightly higher and needs to be more precisely identified (Delque-Količ et al., these proceedings).

Concerning the AMS facility, Artemis has been simulated coupling the ion beam profiler code TRANSPORT (Brown et al. 1980) and the Monte Carlo toolkit GEANT4 (Agostinelli et al. 2003). The most sensitive parts of the spectrometer have first been identified. The resulting TRANSPORT simulations show that the 3 carbon beam emittances have the same behavior and still remain lower than all elements apertures. Then, the trajectories and interactions of the carbon ion beams across the elements along the beam line were modeled with the GEANT4 simulation toolkit, taking into account the physical processes involved: magnetic and electric deflections, energy loss, and straggling. The resulting simulations deduce setting tolerances on 3 main parameters: electric and magnetic fields, pressure, and acceptance values.

Specific research is done at the Artemis facility. The LMC14 team is involved in particular archaeological studies. The first program was performed in collaboration with C Bronk Ramsey of the Oxford Radiocarbon Accelerator Unit (ORAU). It led to a new proposal for the absolute chronology of ancient Egypt. Thanks to historical and archaeological documents, a relative chronology of the kings has been built. Adding some astronomical points and synchronisms from historical texts, it has provided anchor points that have led to some propositions of absolute chronology. ^{14}C measurements were performed with Artemis on Egyptian short-lived materials such as textiles, plants, etc. and attributed to a particular reign or a precise period. Three campaigns of sampling at the Louvre Museum (Département des Antiquités égyptiennes) have allowed us to obtain ~100 measurements on objects coming from the 18th Dynasty. With a Bayesian approach, these analyses have been combined with the known succession and length of the reign. Also, astrological and lunar dates have been recalculated to be incorporated as a prior in the model. Such a model leads us to propose an absolute chronology for this dynasty (Bronk Ramsey et al. 2010; Quiles et al. 2013).

A second research program in progress concerns the ^{14}C dating of ancient iron. This work is done in collaboration with P Dillmann and S Leroy from the Laboratoire Archéomatériaux et Prévision de l'Altération (LAPA). At least until the 19th century, charcoal was used to reduce iron ore into metal. During the reduction process, the carbon present in the charcoal diffuses into the metal of the ferrous alloys. It is therefore possible to ^{14}C date the ferrous archaeological objects. Thus, the carbon in ferrous metals gives the possibility to deduce the age of wood fragments used for the reduction and, therefore, to specify the age of metal since these fragments correspond to relatively young wood. The limitations of the method for reliable dating are mainly due to the small amount of carbon in the raw material. First, except cast iron, ferrous alloys are highly heterogeneous materials with often low carbon concentrations: a soft iron contains less than 0.02% of carbon by weight while an hypereutectoid steel contains more than 0.8% mass. Secondly, there may be sources of pollution from the geological nature of the fuel or the iron ore (siderite $FeCO_3$) that could introduce a bias in the dating. The ultra-small sample preparation and measurement methods developed at the LMC14 laboratory make it technically possible to work with samples of a few mg. Coupling this analytical method with the archaeological data opens up new perspectives for archaeological and historical studies. A special feature of this approach is to undertake a metallographic study of the object to determine the distribution of carbon and target the areas most carburized. Archaeological objects with different carbon contents and of known dates were dated. These data are supplemented by results obtained on iron alloys from experimental smeltings with contemporary charcoal but with carbonate minerals. This methodology can be directly applied to the ^{14}C dating of iron used in medieval Gothic buildings.

CONCLUSION

The Artemis AMS facility of the LMC14 laboratory in Saclay, France, has routinely measured ^{14}C samples since 2003. Over 30,000 samples have been analyzed by Artemis. The performance, in terms of quality reached, is what can be expected from such an AMS facility initially devoted to numerous routine measurements. Since 2008, the Artemis team has been developing specific research and technical development programs to support the routine measurement and to maintain the quality of the results at a very high level. Intercomparison campaigns are often performed on various fields of research and show that the Artemis AMS facility combined with the preparation and graphitization techniques used at the LMC14 laboratory give high-quality data that are compatible with the international standards.

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