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RADIOCARBON DATING ON *ECHO*MICADAS, LSCE, GIF-SUR-YVETTE, FRANCE: NEW AND UPDATED CHEMICAL PROCEDURES

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ABSTRACT. The Laboratoire des Sciences du Climat et de l'Environnement (LSCE) has operated a radiocarbon dating laboratory for almost 70 years. It has evolved from a traditional ß-decay counting to an accelerator mass spectrometry facility. In 2015, the LSCE received a major upgrade with the installation of a MICADAS. This evolution required adjustments in sample preparation to match the new capability to date samples as small as a few tens of µgC. We summarize here the sample cleaning procedures and the chemical purification or extraction treatment that we apply to the samples. We also report values of blank and reference materials of different matrices that match the large diversity of samples handled at LSCE.

KEYWORDS: ^{14}C dating, chemical treatments, *ECHo*MICADAS.

INTRODUCTION

The Laboratoire des Sciences du Climat et de l'Environnement (LSCE), formerly the Centre des Faibles Radioactivités (CFR), hosts a very long-running radiocarbon (^{14}C) dating lab currently in operation. The story began in the early 1950s with a laboratory established in Fontenay-aux-Roses and then in Gif-sur-Yvette (lab code Gsy-) under the lead of Jean Coursaget and experiments carried out at Saclay (lab code Sa-) under the co-responsibility of Georgette Delibrias and Jacques Labeyrie. With the creation of the CFR, the two teams were brought together on the CNRS campus in Gif-sur-Yvette (lab code Gif-). The very first ^{14}C dates were obtained in 1954 on a wood sample from New Caledonia (Gsy-1) and in 1956 on a sarcophagus from the temple of Luxor (Sa-1) then on the Angkor Temple (Sa-2) (^{14}C ß-counting database). The following results were then quickly published as data lists (Delibrias et al. 1964; Coursaget and Le Run 1966). The first Gif- measurement occurred in 1966 with the number 315 that took into account the samples previously measured under both the Gsy- and Sa- codes. The ^{14}C team operated a conventional ß-counting facility in Gif-sur-Yvette until 2008 and an underground ß-counting facility in Modane running between 1990 and 2000 (Fontugne et al. 2021). Meanwhile a 3MV Tandetron accelerator was obtained from High Voltage Engineering in 1982 leading to another radiocarbon unit using the lab code GifA- (Arnold et al. 1987). The two units were combined in 1998 soon after the creation of the LSCE, and over the ensuing decades, the LSCE gradually migrated toward making measurements by accelerator mass spectrometry (AMS) only. Because the ß-counting laboratory undertook the first datings of the Laschamps lava, the Lascaux cave, the Anatolian neolithic tell of the Çatalhuyuk settlement, a stripe from Ramses II mummy, the ancient Semitic city-state of Mari, and many other exceptional sites, its testimonial and patrimonial value is today in the hands of

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the Musée du Conservatoire National des Arts et Métiers, Paris, that hosts most of the counters and associated electronics.

In 2003 the research group (GDR) managing the Tandetron was dismantled, leaving behind only the chemical preparation units in operation and leading to a transfer of technology on the design of lines and the know-how in chemistry towards to the French national facility of ^{14}C measurement (LMC14). The LSCE ^{14}C research unit regained its autonomy of physical measurement in 2015, with the acquisition of a 200 kV Compact Accelerator System dedicated to ^{14}C dating, a Micro Carbon Dating System (MICADAS; Synal et al. 2007). It was named *ECHo*MICADAS, for Environment, Climate and Human (Environnement, Climat et Homme in French) but also in reference to the numerous applications for funding that had be written to obtain the full funds necessary for the acquisition, which *ECHoed*. This equipment was acquired in collaboration with AASPE[1] and GEOPS[2] (Tisnérat-Laborde et al. 2015). The acquisition resulted in a surge of scientific activity and a new era for GifA- numbers: GifA-numbers have since been assigned to sample registration and chemical preparation, while an ECHo-numbers inventories physical measurement. In 2018, the LSCE left the Gif-sur-Yvette building in the valley for the Saclay Plateau but kept the same postal address, thus allowing the ^{14}C dating lab to keep the code GifA- for the chemical preparations.

The LSCE produces about 2000 ^{14}C measurements annually for about 700 samples (inc. replicates), a number that is expected to increase over the coming years as a result of the advancement of the laboratory and of the diversification of the studies undertaken by the lab's researchers. Figure 1 gives a breakdown of the main sample types that will be discussed in this paper.

This paper presents the LSCE ^{14}C lab chemical infrastructures and the associated results for large samples, i.e., higher than 400 µg C when measured on the solid source of *ECHo*MICADAS and more than 60 µg C when measured on its gas source. More information regarding *ECHo*MICADAS and the handling of small samples is given in Tisnérat-Laborde et al. (2015) and in the companion paper, Thil et al. (submitted), respectively.

EQUIPMENT

The LSCE operates the following instruments and apparatus for ^{14}C dating:

- *ECHo*MICADAS (Synal et al. 2007)
- EA-GIS (Ruff et al. 2010)
- EA-AGE3 (Wacker et al. 2010)
- CHS-GIS (Wacker et al. 2013)

See the companion paper (Thil et al. submitted) and Tisnérat-Laborde et al. (2015) for details about the instruments.

- An Elemental Analyzer (EA), Thermo FlashEA1112, for C and N content evaluation.
- An Isotopic Ratio Mass Spectrometer (IRMS), Thermo Delta+XP, connected to the previous EA for $\delta^{13}C$ and $\delta^{15}N$ evaluation.

[1]AASPE : Archéozoologie, Archéobotanique - Sociétés, Pratiques et Environnements, Paris – joint unit of MNHN and CNRS.
[2]GEOPS : Géosciences Paris Saclay, Orsay – joint unit of Université Paris-Saclay and CNRS.

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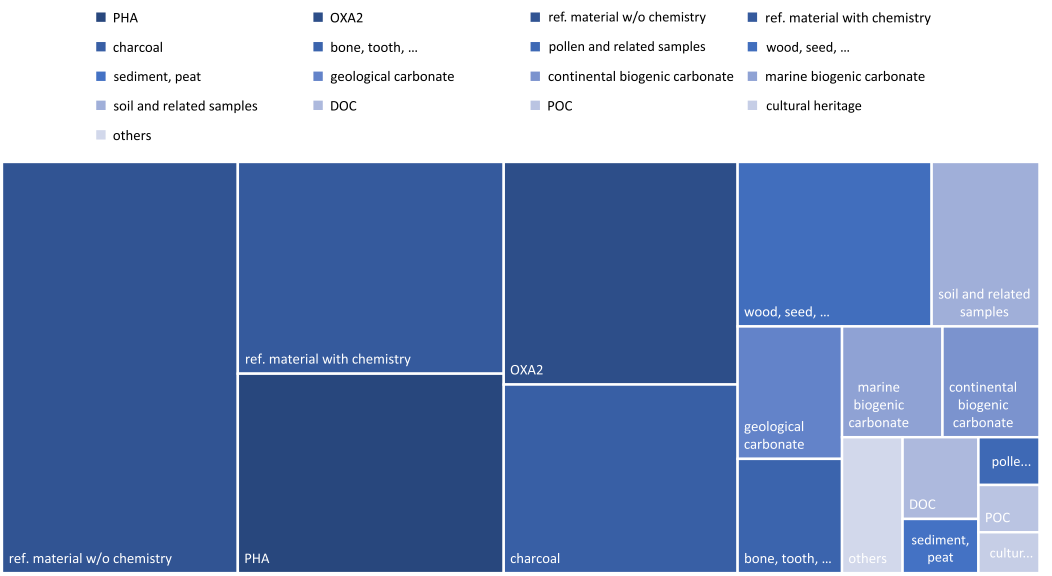

Figure 1 Typical yearly distribution according to the sample types (numbers are those of 2021). "Others" accounts for dissolved inorganic carbon, specific compound specific, aerosols and tests to set up new procedures.

- A pneumatic sample press to press graphite cathodes.
- A Mettler automatic balance, "Epatant". The Mettler XPE206PR automatic balance saves a great deal of time and ensures a higher reproducibility. It is used for all standards without chemistry and for iron weighting, two conventional µg balances and two conventional mg balances, and three binocular loupes.
- An automated graphite line, "Gégé", able to run seven CO_2 reductions at a time, twice a day. It is dedicated to samples whose CO_2 conversion must be done manually (Tisnérat-Laborde et al. 2015).
- Ten homemade glass lines dedicated to the conversion of samples into CO_2, their purification or their storage. Due to their specificity and the automation of the process, these lines are not constantly operated but they are all kept in good working order to be ready for use as soon as a new project emerges.
  - "µline", previously described in Mendez-Millan et al. (2014), designed for the combustion of minute samples or samples with unknown C content and for the thermal decomposition of carbonaceous material. It allows combustion under pure O_2, on-line purification on Ag, Cu and can also be used for CO_2 purification on CaO as briefly described in Hatté et al. (2008). Clean CO_2 is then sealed in 1 to 3 Pyrex µtubes designed for GIS and enclosing up to 90 to 150 µg C each. A spare ampoule is also available for samples yielding more than 400 µg C-CO_2.
  - "BCA", a semi-automated line dedicated to carbonate hydrolysis. Evolved CO_2 is either collected in ampoules or sealed in Pyrex µtubes (Tisnérat-Laborde et al. 2001).
  - "Degassing bench", to pre-pump carbonate samples before installing them on BCA. The line accepts 2 sets of 5 samples, each set mounted on a ramp that is easy to install and remove from the "BCA". Only two clamps are required to change the series.
  - "H_3PO_4 line" to dry H_3PO_4 before its use on "BCA" or CHS on carbonate samples.

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- Two "manual lines", typical versatile manual lines where almost all types of samples can be run (carbonate, organic material, ninhydrin process . . .). They do not contain any purification step besides cryogenic trapping. CO_2 is collected in ampoule. It is used nowadays for large samples that cannot be run on (semi-) automated devices.
- "micro-macro", a double line with one side for standard and one side for purification. On the standard side, very large CO_2 amounts of standard (carbonate and oxalic acid) can be obtained and stored. Storage is done either in a very large glass balloon or under pressure in a metallic bottle. On the purification side, large and very small amounts of CO_2 can be either cleaned on "Yoyo" containing Cu (Fontugne et al. [2021] or through the "calcite" procedure for large samples, and Hatté et al. [2008] for small samples).
- "DIC sea water", a typical linear line under He flux designed for acidic release of Dissolved Inorganic Carbon (DIC) from water. The current line does not differ much from the original Gif-sur-Yvette line (Bard et al. 1987).
- "Active line", a manual line dedicated to active samples, mostly from nuclear plant area, analyzed in the frame of environmental studies (Tisnérat-Laborde et al. 2021).
- "BMOA", an automated line for organic matter (Hatté et al. 2003) is no longer in use and has been advantageously replaced by EA-AGE3.
- A "DOC" line for UV conversion of marine dissolved organic carbon is under construction.

- Chemical laboratories under pressure equipped with several fume hoods, vacuum ovens, centrifuges, osmosis and ultrapure water and side rooms for every step of chemical treatments.
- Dirt lab for mechanical cleaning (i.e., cutting, abrasion, . . .) and ethanol/dry-ice mixture preparation.
- Laundry to clean all dishes and metal instruments, inc. osmosis water, lab dishwasher, acid bath, ovens to dry and combust dishes.

SAMPLE NUMBERING AND DATA CURATION

Sample numbering is a key for data management and archive sustainability. The system we have designed is a mix between the laboratory tradition of numbering the sample as soon as it arrives at the laboratory and the target numbering procedure in Squirrel, the database associated to MICADAS. It is illustrated in Figure 2. We have set up a system that allows us to account for the number of chemistries that have been applied to the sample (numbered suffix) and the aliquots that it has been possible to extract from the sample. For these, we define differently what is homogeneous from what is heterogeneous. Also, if the initial sample contains two fractions that we want to measure independently, e.g., a water sample on which we want to measure DOC, DIC and POC, then as many GifA-numbers as fractions to be analyzed are given. If, after the chemistry, it is advisable to separate the clean sample into several aliquots, then a numbered suffix is added. If an aliquot is done after the conversion to CO_2 or after the reduction, another suffix is added but as we consider that the CO_2 or $C_{graphite}$ is homogeneous, the suffix is no longer a number but a letter.

We are designing a database that will absorb both historical and new sample data, as well as all the parameters collected at each stage of the process. Today, all of this exists but distributed in several places and in various formats. Each new sample is associated with a list of data collected on a "information sheet" (electronic today and paper in the past, currently being scanned) that

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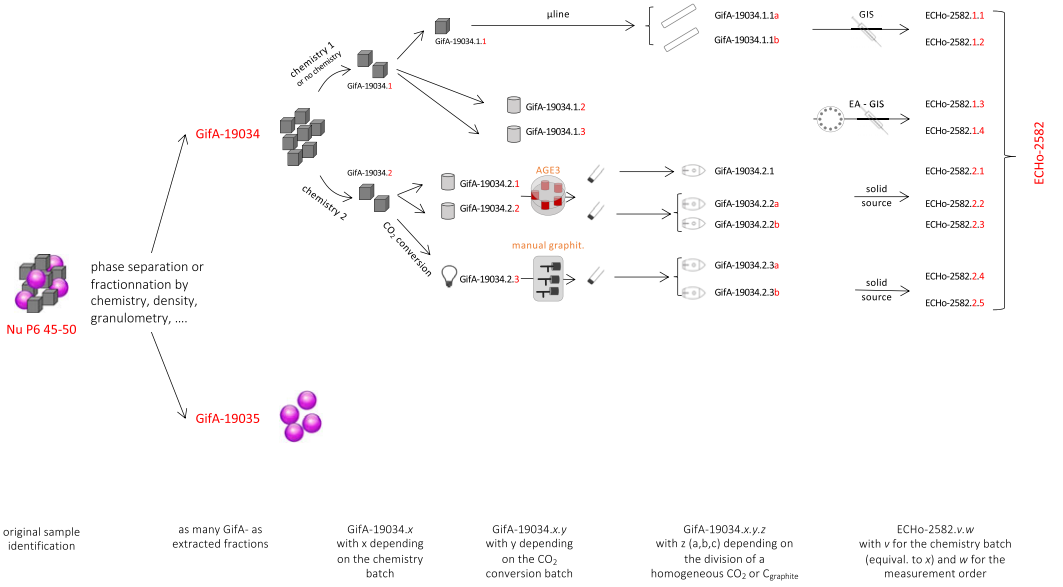

Figure 2 Sample numbering procedure. The GifA- numbering takes into account the number of fractions to be ^{14}C analyzed, the number of chemistries applied on the sample, the number of possible aliquots after chemistry (the sample remains heterogeneous, numbering continues with number), after CO_2 or C conversion (the sample is homogeneous, numbering is then done with letter). ECHo numbering is much simpler: the first suffix is for the chemistry batch (equivalent to x), the second suffix is for the order number of the sample measurement.

is given to us along with the sample. To collect the parameters of all the steps of the dating process and to ensure the quality of the measurements, we have established a data management plan within the framework of the REGEF[3] network. It will be soon publicly released on REGEF website. The information we collect goes beyond the only information we need to adapt chemical treatments. It is a clear commitment to make the database useful beyond the daily life of the ^{14}C laboratory and to give it an intrinsic scientific value. It is not made public beyond the researchers involved in the ^{14}C laboratory, but it can be punctually queried (through us) to find information on past samples.

CHEMICAL LAB ENVIRONMENT

To reduce the risk of contamination, chemical treatments are performed in a pressurized chemical laboratory. Chemical solutions are prepared on the day of use and are not kept for more than 2 days (especially for basic solutions). The water used is ultra-pure water, osmosed and then oxidized by UV. The glassware is cleaned by boiling in EXTRAN® and rinsing in osmosed water and acid. All the glassware, aluminum papers and weighing capsules are burned at 450ºC for 5 hours before being used. After chemistry, the samples are either dried in a vacuum oven at low temperature or freeze-dried in a freeze-dryer at –80ºC. When dry, they are stocked and preserved in dry neutral dry gas (N_2) chambers to prevent just-in-time processes between chemical pre-treatments and ^{14}C analyses (Scott et al. 2007, 2010, 2017, 2019). Weighing times of samples and standards are done with equipment dedicated to each standard, either a spatula or a specific weighing head of the Mettler® automatic balance.

[3]REGEF: Réseau Géochimique & Expérimental Français – French geochemical & experimental network.

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SAMPLE PREPARATION AND RESULTS

Our process consists in framing the samples with two types of reference materials: standards without chemistry and reference materials with chemistry. Standards without chemistry are used to check the correct functioning of the reduction (if any) and the measurement (phthalic acid, oxalic acid 1, IAEA-C7, IAEA-C8, IAEA-C3, and VIRI O cellulose, VIRI U humic acid) and to ensure the normalization of the measurements (oxalic acid 2). The reference materials are used to verify the effectiveness and innocuity of chemical treatments. These reference materials are made of the same material as the samples and are either blanks or have a similar age to the samples. They are either international standards, reference material from intercomparison projects (e.g., Scott et al. 2007, 2010, 2017, 2019) or internal standards from the ß-counting period, that have been measured many, many times. The results we have obtained on these reference materials are presented here.

First Check and Typical Physical Pretreatment

All samples, regardless of material, are examined under a binocular loupe. Working with MICADAS, i.e., with quantities of carbon as small as a few tens of micrograms, requires great precautions. A hair of a sweater, one millimeter of hair, is 5 µg of carbon. It might lead to a rejuvenation of ~2500 ^{14}C years on a 100 µg C sample of 30 kBP or of ~200 ^{14}C years on a 100 µg C sample of 10 kBP. Moreover, it turns out that examination at this scale sometimes allows the material to be dated to be discretized: a carbonaceous ensemble may turn out to be a mixture of charcoal and unburned seeds, or plant excrement may contain µcharcoal that could potentially come from upper stratigraphical layers and would be better dated separately. This first examination allows for the correct selection of the dating support. When needed, mechanical abrasion is performed using a Dremmel® tool.

Charcoal and Wood (Bulk) Preparation

Acid-alkali-acid (AAA) treatment is commonly performed using HCl 1N and NaOH 0.1N. The chemistry is performed in a glass centrifuge tube, and solution removal is done with a Pasteur pipette.

Charcoal is typically treated at room temperature, while wood is cleaned at high temperatures to allow the small bubbles to work their way into the wood's pores and remove any contaminants more effectively. Rinses are repeated until the pH of the water is restored to the one of ultrapure water. The rinsing after the basic treatment is the most critical, as the subsequent acid treatment could precipitate "organic contaminant residues" (formerly called humic acids) and lock them in the sample mass. The duration and the number of steps differ with the sample. Several short alkaline treatments are preferable to one long treatment in the same solution as at the start. As soon as the color changes, the solution is removed, or collected to date humic acid, and replaced by a new one, sometimes at a lower concentration and after a rinsing step if the sample has reacted strongly. Samples that are a priori fragile are treated by gradually increasing the concentration of NaOH. The specific case (unbreakable ionic bond formed during the alkali step between some functional groups of organic sample and bicarbonate from modern carbon dissolution) reported by Hatté et al. (2001a) remains very rare.

The charcoals pigments of rupestrian paintings have long been investigated by our lab (Valladas et al. 1992) and are the focus of attention. They are small and very fragile and are

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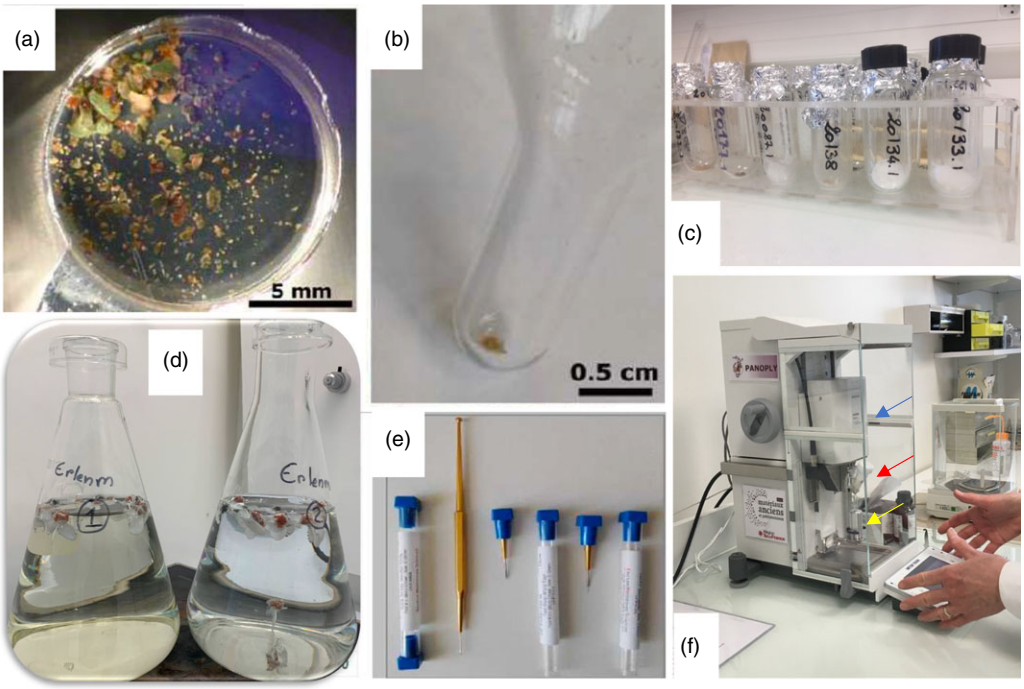

Figure 3 Some photos to illustrate the LSCE ^{14}C laboratory: (a) pigment and varnish in a pre-combusted Aluminum cup; (b) selection of 200 µg of colophony varnish in a tube with excrescence; (c) collagen in centrifugation tubes from bones after a modified Longin protocol; (d) two Erlenmeyers, each with 15 samples and 5 reference materials in individual disposable Teflon bags; (e) set of hard steel microchisels with different sizes of tool tip 0.120 mm, 0.25 mm, 0.5 mm and handle; (f) automatic balance (the red arrow points to the interchangeable head (one head per reference material or iron), the red to the vibrating motor, the green to the container holder (here a AGE3 reduction tube).

often associated with mineral particles and other material. The general line of the chemical treatment remains the same, i.e., AAA treatment, but the chemical concentration is adapted, and most often reduced. As the residue after chemistry sometimes still contains minerals, it is difficult to assess a priori the quantity of carbon that remains available for combustion and hence to divide it correctly between several capsules to be sent to the EA-GIS system, i.e., by ensuring ~100 µg of carbon per capsule. In this case, the sample is oxidized with pure oxygen on the "µline" where the gas obtained can be conditioned in one or several µtubes of ~100 µg C each to optimize the measurement.

To transfer the sample into the quartz tubes required for the µline, we use a specific container. It is a centrifuge tube extended by a quartz tube of about 1 cm, forming an excrescence (Figure 3b). The sample is directed with a minimum of water in the bottom of the excrescence. A very fine metal rod with a twist at one extremity is plunged into the bottom of the tube. The whole is frozen in liquid nitrogen. The water forms a block of ice, trapping the sample and the metal rod. By slightly heating the excrescence with the hand, the ice block melts a little and it is possible to extract it from the tube by pulling on the metal rod. The ice and the sample can then be transferred in a combustion tube of the µline. The sample is then dried in the combustion tube in the vacuum oven.

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The reference materials we use the most frequently are listed in table 1. We also punctually use other charcoal and wood reference materials made available by the intercomparison exercises (e.g., SIRI H). The results we obtained over the last two years on our blank reference materials (the "AfSud" charcoal and three different woods: "El Akarit", "Chiloé", FIRI A) are shown in Figure 4. To illustrate our reproducibility, individual results of two reference materials, a charcoal (Gif1423) and a wood (SIRI E) are shown in Figure 5.

Cellulose Extraction

Cellulose extraction was not a widespread activity in the lab until we decided to participate in the community effort to provide more and more annual ^{14}C records from tree rings. It was then no longer possible to use our conventional, time and labor consuming procedure. We therefore investigated another solution. Our new procedure, called "batch procedure", derives from the protocol used for stable isotope measurements at LSCE which in turn derives from the original protocol of Leavitt and Danzer (1993). We also followed some recommendations made by Southon and Mangana (2010) and added our own "touch".

The chemistry is done in a 1.5 L Erlenmeyer flask in which the samples and standards are pooled, packed in an individual Teflon bag. The protocol is divided into three main steps: removal of water-soluble compounds, removal of lignin by a two-step oxidative delignification and removal of hemicellulose by alkaline extraction.

- From 7 to 8 mg of wood (sample and reference material) are cut into small chips. The mass depends on the species which can show different extraction yields.
- The single use Teflon bag is made of a 47mm Teflon disc with 10-µm pores, a Teflon label with engraved number and Teflon string.
- The Teflon bags are boiled for 6 hr in ~1 L ultra-pure water in a 1.5 L Erlenmeyer. The water level is adjusted to ensure at least ~0.5 L of water in the recipient.
- The Teflon bags are then transferred into a 1 L Erlenmeyer, covered with watch glass, filled with 100 mL of ultrapure water, 2 mL of 0.5N HCl and 100 mL of 10%wt $NaClO_2$ where they stay overnight at 70–80ºC. The volumes are defined to reach the right level of acidity and oxidizing strength.
- The following morning 25 mL of water, 10 mL of 0.5N HCl, and 25 mL of 10%wt $NaClO_2$ are added. 10 mL of 0.5N HCl and then 2 mL of 12N HCl are added after 2 and 2 extra hours. This is to maintain an acidic and oxidizing environment throughout the reaction, and overnight at 70–80ºC.
- The following morning, after having been rinsed several times with ultrapure water using ultrasound, the Teflon bags are immersed in 1M NaOH for 1 hr at 70–80ºC, rinsed again, immersed in 0.5N HCl for 1hour at 70–80ºC and rinsed again. Rinsing must be sufficiently repeated for the pH of the water coming out of the bags to be at the ultrapure water pH value.
- Samples within the Teflon bag are dried in a vacuum oven overnight and kept in a dry cabinet until analysis.

Our protocol allows the preparation of up to fifteen samples and five standards at the same time, without cross-contamination, thus saving time in handling and reducing chemical consumption. It lasts 3 days. The reference materials we use to check the reliability of our protocol are the same as for wood bulk.

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Table 1 Results obtained for the most frequently used reference materials with chemistry at LSCE. Data are from the 1.1.21 to 31.10.22 period. The first seven columns give the identification of the materials (name, nature, origin and expected age). They were mostly made available either by intercomparison exercises or from the ß-counting laboratory samples archive. (a) is for Scott et al. 2017; (b) is for Scott et al. (2010); (c) is for $F^{14}C$ retrieved from IntCal20 (Reimer et al. 2020); (d) is for $F^{14}C$ retrieved from Bomb21 (Hua et al. 2022). The following columns are for the results obtained at LSCE lab: the analyzed fraction and the results according to the measurement mode (solid or gas sources) and the introduction methods (EA-GIS, CHS-GIS or cracking-GIS). Only samples larger than 400 µg C for the solid source and larger than 60 µg C for the gas sources are shown here. For every modality, the number of analyzed targets, the $F^{14}C \pm 1$ sigma, the corresponding age in BP are provided. If the reference material is associated to a finite expected $F^{14}C$, the z-test result between the expected value and our results is provided: (*) is for a 1-sigma agreement, (**) is for a 2-sigma agreement, (***) is for a 3-sigma agreement.

reference material characterization				expected value			LSCE result											
								solid source (>400µgC)				gas source (> 60µgC)						
												EA-GIS or CHS-GIS				cracking-GIS			
lab identification	nature	origin	original dating	F14C	age	ref.	fraction	n	F14C	age	z-test	n	F14C	age	z-test	n	F14C	age	z-test
AfSud	charcoal	Border cave (South Africa)	125 kyr (U/Th)	0	infinite		bulk	36	0.0032 ± 0.0007	~46 kBP		16	0.0060 ± 0.0009	~41 kBP		44	0.0048 ± 0.0017	~43 kBP	
Gif6158 - 1	charcoal	Boqueirão da Pedra Furada (Brazil)	ß-counting	~0.008	~38.8 kBP		bulk	7	0.0082 ± 0.0017	38,587 ± 1,690		3	0.0103 ± 0.0010	36,756 ± 782					
Gif6158 - 2	charcoal		ß-counting	~0.018	~32.3 kBP		bulk	6	0.0192 ± 0.0007	31,755 ± 293						9	0.0193 ± 0.0013	31,711 ± 542	
Gif1453	charcoal	Jbel Ouam (Morocco)	ß-counting	~0.5			bulk	16	0.4906 ± 0.0031	5720 ± 51		5	0.4889 ± 0.0053	5748 ± 87					
Chiloe	wood	Argentina	blank (14C ß-counting)	0	infinite		bulk	6	0.0026 ± 0.0007	~48 kBP		4	0.0062 ± 0.0007	~41 kBP			-		
							cellulose	2	0.0033 ± 0.0010	>46 kBP		4	0.0072 ± 0.0007	~40 kBP			-		
El Akarit	wood	Oued el Akarit (Tunisia)	blank (14C ß-counting)	0	infinite		bulk	4	0.0025 ± 0.0004	~49 kBP		2	0.0066 ± 0.0003	~40 kBP			-		
							cellulose	3	0.0038 ± 0.0003	~45 kBP			-				-		
FIRI A	wood	intercomparison	blank	0	infinite		bulk	3	0.0046 ± 0.0005	~43 kBP			-				-		
SIRI E	wood	intercomparison		0.2593 ± 0.0002	10843 (6)	a	bulk	10	0.2594 ± 0.0017	10840 ± 53	*	2	0.2564 ± 0.0027	10933 ± 85	**				
							cellulose	1	0.2581 ± 0.0016	10880 ± 50	*		-						
FIRI D	wood	intercomparison		0.5705 ± 0.0002	4508 ± 3	a	bulk	4	0.5706 ± 0.0003	4507 ± 3	*		-						
FIRI H	wood	intercomparison		0.7574 ± 0.0005	2232 ± 5	a	bulk	4	0.7579 ± 0.0018	2227 ± 19	*		-			1	0.7544 ± 0.0060	22264 ± 64	*
							cellulose	3	0.7569 ± 0.0019	2237 ± 20	*		-						***
SIRI G	wood	intercomparison	dendro - AD1479	0.9539 ± 0.0006	377 ± 5 BP	a	bulk	10	0.9543 ± 0.0025	376 ± 21	*	3	0.9574 ± 0.0015	350 ± 13	***				
							cellulose	2	0.9536 ± 0.0020	382 ± 17	*		-						
MAGC63	wood	British Museum	dendro - AD1586	0.9593 ± *0.0012*	334 ± *10*	c	bulk	1	0.9602 ± 0.0025	326 ± 21	*		-			1	0.9589 ± 0.0064	337 ± 54	*
							cellulose	3	0.9582 ± 0.0027	343 ± 23	*	2	0.9624 ± 0.0036	308 ± 30	*		-		
bois St Pierre	wood	Beaucamps-le-Vieux (France)	~AD1969	1.53 - 1.60		d	bulk		-			1	1.5513 ± 0.107				-		
							cellulose	4	1.5668 ± 0.0024				-				-		
A2 mammoth	mammoth bone		blank	0	infinite		Longin	15	0.0035 ± 0.0009	~45 kBP		7	0.0086 ± 0.0012	~38 kBP			-		
VIRI I	whale bone	intercomparison		0.3545 ± 0.0003	8331 ± 6	b	Longin	2	0.3525 ± 0.0007	8376 ± 16	***	2	0.3548 ± 0.0005	8324 ± 11	*		-		
VIRI F	horse bone	intercomparison		0.7314 ± 0.0005	2513 ± 5	b	Longin	5	0.7312 ± 0.0023	2515 ± 25	*	2	0.7223 ± 0.0054	2503 ± 59	*		-		
Cheval d'Orléans	horse bone	Orléans (France)	archeo ~mid 13ème s.	~0.90		c	Longin	3	0.9039 ± 0.0027	812 ± 24		1	0.9069 ± 0.0069	785 ± 61			-		
IAEA C1	marble	IAEA	blank	0	infinite	IAEA	bulk	25	0.0016 ± 0.0004	~52 kBP		32	0.0040 ± 0.0014	~44 kBP		40	0.0026 ± 0.0010	~48 kBP	
IAEA C2	marine turbidite	IAEA		0.4114 ± 0.0003	7135 ± 6	IAEA	bulk	11	0.4102 ± 0.0018	7158 ± 35	*	4	0.4130 ± 0.0023	7104 ± 45 BP	*	17	0.4118 ± 0.0037	7127 ± 72	*

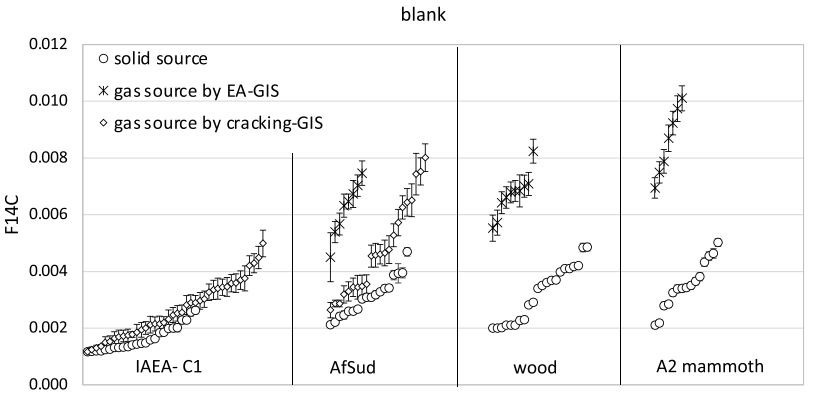

Figure 4 $F^{14}C$ (±1σ), ranked in ascending order, obtained on blank reference materials for the 1.1.21–31.10.22 period. The figure shows the results obtained on the solid source (circle) either after AGE3 or Gégé graphitization, the results obtained on the gas source through EA-GIS (star) and tube cracking-GIS (diamond) introduction after either the µline or the semi-automated carbonate line. Only samples larger than 400 µg C for the solid source and larger than 60 µg C for the gas sources are shown here. Results are for the IAEA-C1 carbonate, the AfSud charcoal, the A2 mammoth bone collagen and cellulose and bulk organic matter of "El Akarit", "Chiloé", FIRI A woods (all together). We handle three blank woods that were preserved in different environments and thus were subjected to different contaminations. This makes it possible to better match the blank to the specificities of the sample set.

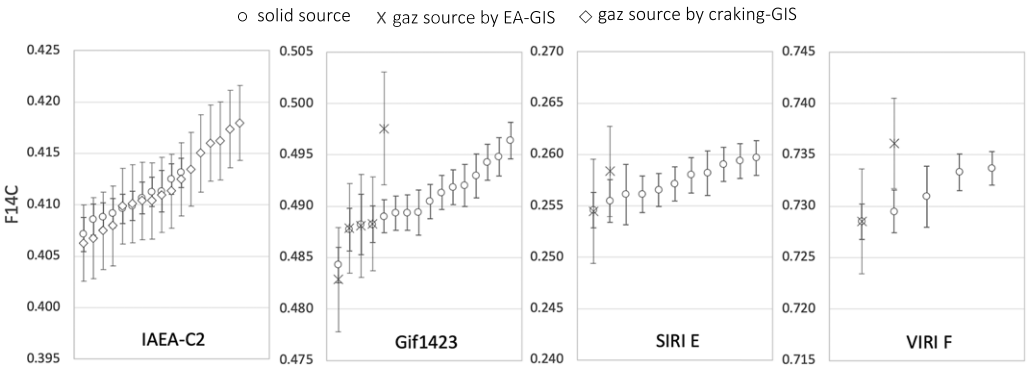

Figure 5 $F^{14}C$ (±1σ), ranked in ascending order, obtained on three reference materials commonly used at LSCE, for the 1.1.21 – 31.10.22 period. The figure shows the results obtained on the solid source (circle) after AGE3 (organic material) or Gégé graphitization (carbonate) and the results obtained on the gas source through EA-GIS (cross) introduction or cracking-GIS (diamond). Only samples larger than 400 µg C for the solid source and larger than 60 µg C for the gas sources are shown here. Results are for the IAEA-C2 carbonate, the Gif1423 charcoal, SIRI E wood and the VIRI F bone collagen.

Carbonate Preparation

Before being installed either on "BCA" or CHS, carbonate is pre-treated to remove any possible recrystallisation. In a generic way, the chemical treatment can be summarized as "HNO_3 leaching" (Tisnérat-Laborde et al. 2001) but in practice, it differs according to the sample type: thin or thick biogenic structural carbonate, biogenic excretion carbonate or geologic carbonate.

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Thin biogenic structural carbonate, such as that from pteropods or foraminifera and especially benthic foraminifera, is treated with caution. Shell or test may be crushed to allow efficient chemical treatment on all surfaces. If required, such samples are first cleaned in ultra-pure water to get rid of sediment. The duration of this step is kept as short as possible as with a pH of 5 ultrapure water begins to destabilize carbonate ($pKa_1 \sim 6.4$). A weak acidic and oxidizing treatment is then done with 0.01N HNO_3. A rinsing step is applied on the largest samples but not to the smallest ones. Samples are then connected to the "degassing bench" to be dried on line. The HNO_3 treatment is applied within the vial for samples in CHS.

Thick biogenic structural carbonate, such as coral and mollusk shell, is first pre-cleaned by sand blasting until elimination of secondary crystallization in skeleton pores or surficial contaminants (Paterne et al. 2004). Once rinsed and ultrasonically cleaned, the sample is crushed in an agate mortar or sampled at a regular spacing with a MicroDrill. The chemical treatment is similar to those described above but may be longer or be performed with a higher concentration of HNO_3, depending on the sample (size and crystalline structure).

Calcium carbonate from plant parenchyma cells is very fragile, often presented in microsphere clusters, and is treated with the same precautions as benthic foraminifera.

Biogenic excretion carbonate such as earthworm granules (Moine et al. 2017) and geological carbonate such as speleothems show a more robust structure and HNO_3 leaching is done with 0.1N HNO_3 with a longer contact time. The risk of losing too much targeted material is much lower and the procedure is thus intensified to ensure total dissolution of potential recrystallisation and more efficient surrounding organic matter oxidation. Particular attention is paid to speleothem powders resulting from a MicroDrill, which can lead to heating of the carbonate crystalline structure and therefore contamination by atmospheric $^{14}CO_2$ during sampling.

The most frequent reference materials are shown in Table 1. They are completed with a coral blank and a speleothem blank that we did not use during the period summarized in the table. We also ask sample providers for a blank from the marine or lacustrine core to be studied. It consists of carbonate from the same species as the series to be dated but that is beyond the ^{14}C- dating limit and if possible, even older than 100 kBP. This series is currently expanding to provide a better temporal coverage and to be closer to the carbonate structure of samples. Note that if the reference material is carbonate but not of the same origin as the sample series, it undergoes the same chemical treatment as the samples. See Figure 4 and 5 for results on IAEA-C1 blank and IAEA C2, respectively.

Organic Matter from Soil and Sediment

The preparation of soil and sediment differs according to the objectives of the study, i.e., whether an understanding of paleoclimatology or of the carbon cycle is sought. Amino acid and amino sugar are important components of the carbon cycle and must be preserved during the sample processing, whereas they can be considered as contaminant from modern microorganisms growing on the sediment when it comes to paleoclimatology.

Sediment and soil samples for paleoclimatological purposes are decarbonated if necessary, according to Gauthier and Hatté (2008). Particular care is taken during the settling phase (acid step and rinsing) to avoid losing the fine fraction which is the principal support of organic

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carbon, and the drying temperature is carefully regulated to avoid destabilizing organic matter that has been made more fragile by chemical treatment.

Current knowledge on organo-mineral interactions shows that the organic molecules pile up on each other with the mineral surface as a basic support (e.g., Kleber et al. 2007). If the clays in the sediment have had another life before being deposited at the core site (fluviatile or lacustrine deposits, loess...), it is likely that the mineral-bounded organic matter is not contemporaneous with the event to be dated but is a phantom of the previous context. If the transit time between resuspension and deposition of mineral grains is not long enough or is not conducted under sufficiently oxidizing conditions, the original mineral-bounded organic matter is not eliminated by biological consumption or oxidation and will be part of the bulk sediment organic matter, together with the organic matter that results from autotrophic production at the coring site. When subjected to an acid treatment, some organic matter in the periphery will be eliminated. These are mainly amino acids and amino sugars, which are the constituents of what was formerly called "humic acids". "Last in, first out", these eliminated organic matters are often the most recent. They leave behind a residue with an apparent age older than the initial total organic matter, which we call "perfect bulk". By adding a basic treatment, the chemistry attacks deeper layers. The residue after chemistry, which used to be called "humin", has an even older apparent age compared to the original age. That is why the previously named "humin" is very often older than "humic acid" and why the (real) "perfect bulk" is in between. So, when applying an alkali step, we caution that the fractions obtained in the chemistry room are unlikely to fit the different possible sources of carbon, but that the difference between ^{14}C datings may just give an idea of the range of ages expected in the mixture.

Based on this new knowledge of organo-mineral interaction, loess dating as previously advocated (Hatté et al. 2001b) is re-evaluated according to the geomorphological context. The protocol works well in the Rhine Valley where dust transport (fine fraction) is long enough to allow almost complete oxidation of the organic material that was originally associated to the dust. The loess organic matter, in this context, is thus that of the plants that trapped the dust. Hatté et al.'s (2001b) protocol cannot be used as such, however, for dating the Great Plains loess section (USA) because the moraines, which are the source of dust, are too close to allow a high predominance of organic matter contemporaneous with loess formation. Rather, it reflects both trapping of moraine-trapped ancient organic matter and loess formation (unpublished data).

Carbonaceous sediment and soil samples for carbon cycle understanding purposes are decarbonated in capsules without any rinsing step or removal of aqueous solution. Amino-acid and amino-sugar should be kept within the sample and the soluble part that goes into the acid solution must remain part of the analyzed sample after the leaching. Sediment or soil carbonate content is evaluated thanks to two carbon content and $\delta^{13}C$ measurements: one on bulk sediment, the second on sediment leached in the capsule. Decarbonation is done under a binocular loupe. Based on the carbon content evaluation, the amount of material to achieve a proper $\delta^{13}C$ evaluation in the best conditions is weighed in two Sn capsules. One is closed, while the other one is placed under a binocular loupe where decarbonation can be closely monitored: 10 to 20 µL of 1N HCl is added to the sediment. If the amount of sediment is large, water can be added to wet the sediment and ensure proton diffusion throughout the whole sediment. The 1N HCl addition is repeated if bubbling or suspicion of bubbling is noticed. About 30 min later, an additional 10 µL of 1N HCl is added. Capsule and solution are frozen then freeze-dried and closed. Decarbonation is then performed as soon as possible before the IRMS measurements. 1 to 2 days delay can be managed by storing the capsules in a dry cabinet under dry neutral gas

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flow or by leaving them in the freeze-dryer. HCl salt is hydrophilic and tends to capture water to reform liquid HCl that reacts with Sn to form SnCl and fragilize the capsule. Based on carbon content and $\delta^{13}C$ before and after the decarbonation, the mass of material to be sampled to obtain 100 µg of C for EA-GIS or 1mg of C for AGE3 and the volume of 1N HCl to be added for complete decarbonation is evaluated. We repeat decarbonation in the capsule as previously done. The volume of added HCl is restricted to a minimum to bring three folds of the required protons. This is done to limit the quantity of Cl^-, which is a poison for graphitization and makes the capsule fragile and less easy to manipulate.

Reference materials do not exist for soil and sediment samples. We thus use standards without chemistry to check the combustion, reduction, and measurement.

Bone Treatment

Bones are prepared in two ways: (1) a modified Longin protocol to extract pure collagen, and (2) the ninhydrin protocol to extract one specific carbon from the proteins embedded in the bone structure (Tisnérat-Laborde et al. 2003). The latter requires more material than the former and is much more time-consuming. Collagen extraction is therefore the most common protocol used in the lab. It derives from the original Longin protocol (Longin 1971), appropriated a long time ago by the Gif ß-counting lab and adapted to the small amounts of material now run on *ECHo*MICADAS, benefiting from tips of our sister labs (Cersoy et al. 2017; Richardin et al. 2017).

Prior to any treatment, the bone organic carbon content is evaluated for nitrogen content. We typically run samples with nitrogen content higher than 0.5%wt. Using the Ambrose (1998)'s relationship: $\%C_{th} = 2.7\ \%N + 1.4$, this corresponds to a theoretical organic carbon content higher than 2.7%wt.

The chemical treatment follows the cleaning step done to ensure the elimination of any material that may contain proteins and polypeptides. The bone sample is then crushed to a fine powder using a glass mortar and pilon; these are preferred to a planetary mill to restrict the risk of contamination and loss of powdered sample adhering on the bowls. The first chemical step consists in decarbonation of the bone powder with 0.6N HCl. Acid is regularly added and pH checked to ensure a pH=1–2 environment. The leaching is done at 4°C. This step can last for 2 to 4 days. The bone powder is then rinsed with ultrapure water until pH=5. The rinsing steps are performed with centrifugation. Particular care is taken during the solution removal step with a Pipette Pasteur to be sure not to remove proteins that may already be outside the mineral structure. An alkali step follows with 0.01 to 0.1N NaOH at room temperature for 30 min or at 4ºC for 2 days depending on the sample. Several short alkali treatments may be required for some bones, especially those from a humid environment and this is preferred to a long unique alkali step. A rinsing step to retrieve a pH of 5–6 then follows. The next step consists in protein hydrolysis. It is done with 0.001N HCl (pH=3) at 80–90°C for about 12 hr. The acidic solution contains the collagen proteins. If the sample treatment yields a lot of mineral residues (phosphate?), the solution is filtered on a pre-combusted GF/F filter folded in a glass funnel or is filtered using a syringe equipped with a pre-combusted APFC filter. As filtration often results in a loss of material, it may be decided to carry out the separation between collagen and residue after the freeze-drying. The solution is thus left as it is, frozen and freeze-dried. The separation between clean collagen filament and the powdered residue is then done manually under a binocular loupe. The carbon and nitrogen content of the collagen, a white to yellowish fluff, is

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then analyzed to specify its purity. $\delta^{13}C$ and $\delta^{15}N$ are not systematically measured and are only performed for a specific purpose. If there is enough material and scientific or analytical interest, Fourier-transform infrared spectroscopy (FTIR) evaluation can be done.

The reference materials in use are shown in Table 1, the individual results on blank in Figure 4 and on VIRI F in Figure 5.

Organic Carbon from Water Samples

Dissolved Organic Carbon (DOC)

In the field, water samples are filtered using pre-combusted GF/F filters and stored in cleaned (acid washed and combusted) amber glass bottles. Additional filtration at 0.45µm can be added to strictly comply with the definition threshold for dissolved materials. The DOC fraction of organic rich water (DOC > 1g/L) is then retrieved by freeze-drying. About 200 mL of water are frozen in a thick-walled 400 mL glass beaker and then freeze-dried. The remaining powder contains both dry DOC and mineral carbonate. As for soil, the dry matter is decarbonated in capsules following the same protocol based on a carbonate content evaluation that derives from $\delta^{13}C$ measurement before and after strong decarbonation. If provided, $\delta^{13}C$ of dissolved inorganic carbon can also be used to evaluate the amount of carbonate to be removed. Based on the carbonate content estimate, the amount of HCl to be added is evaluated. Decarbonation is done under a binocular loupe.

Particulate Organic Carbon (POC)

Particulate Organic Carbon is retrieved on field by filtering water on pre-combusted GF/F quartz filter. Filters are dried as soon as possible at low temperature (50ºC). In the laboratory, the filters are repositioned on the filtration bench to be decarbonated with HCl 0.6N and rinsed with ultrapure water. The decarbonated filters are again dried at low temperature. A punch is taken to evaluate the amount of carbon present on the filter, the C/N ratio and the $\delta^{13}C$ isotopic composition. Depending on the organic load of the water, the punch can have a diameter of 2, 4, 6, 8 mm or more. Based on this result, the punch diameter to be sampled to obtain 100µg of C for EA-GIS or 1mg of C for AGE3 is evaluated and the punch is taken. To avoid melting between the glass fibers of the filter and the quartz columns of the elemental analyzer, "false sediment samples" of comparable age are introduced between two filters and/or EA maintenance is carried out as soon as the series of measurements has been completed. As no reference materials for DOC or POC are available, we use standards without chemistry to check the steps that follow the chemistry.

Other Materials Considered for ^{14}C Dating

Dissolved Inorganic Carbon (DIC) and specific compounds are also run at LSCE. No chemistry is required prior to DIC extraction; the modus operandi can be found in Coularis (2016) deriving from Bard et al. (1989). The radiocarbon dating of specific compounds began in 2008 at LSCE with the acquisition of a Preparative Gas Chromatography with Fraction Collector (Prep-GC-FC) used for the ANR Dynamos project (Mendez-Millan et al. 2014). It was involved in the recently launched intercomparison exercise (Casanova et al. 2021).

CONCLUSION

The Radiocarbon Laboratory of the "Laboratoire des Sciences du Climat et de l'Environnement" in Gif-sur-Yvette has a long history dating back to the 1950s and has

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benefited from decades of chemical and physical improvements in ^{14}C dating. The addition of the MICADAS system enabled work to be pursued in environmental, climate and archaeological sciences not only for research projects carried out by the LSCE on its own, but also for scientific collaborations and to meet the needs of the scientific communities who address their samples and scientific questions to the LSCE.

NOTE AND ACKNOWLEDGMENTS

The list of authors includes the names of all permanent staff who have worked with ^{14}C in the last 40 years. By the professions represented (chemist, physicist, glassmaker, electronic engineer, geologist, oceanologist, archaeologist . . .), it illustrates the interdisciplinarity necessary for the setting up and operation of such a laboratory. Unfortunately, the current size of the staff around such a valuable resource has decreased to only three FTE today.

The MICADAS was acquired thanks to the financial support of the Ile-de-France region (DIM ANALYTICS), the BNP Paribas Foundation (FATES project), the European ERDF funds, the LabEx Div and internal resources of the three labs of the consortium. The other instruments mentioned in this article were acquired thanks to funding from the CEA, the CNRS, the Ile-de-France region and the own resources of the LSCE and its sister labs for the shared instruments. The operation of the laboratory is possible thanks to the financial support of CEA, CNRS, and UVSQ for the salaries of the permanent staff and to funds assigned by different research agencies for our own or collaborative research projects.

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