Laboratoire de Mesure du Carbone 14

La datation ^{14}C, ses applications classiques et insolites

Lucile Beck et équipe LMC14

Laboratoire de Mesure du Carbone 14

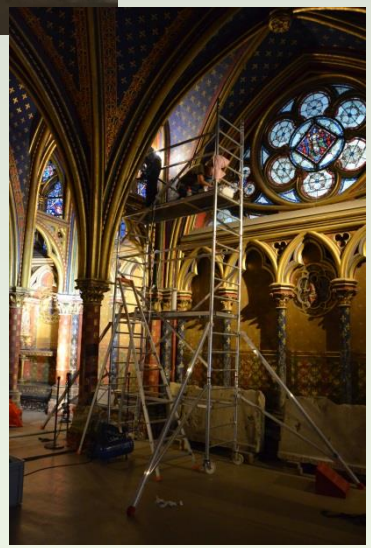
CEA/CNRS/IRD/IRSN/MC-LSCE

CEA Saclay, Bâtiment 450, porte 4E

91191 Gif sur Yvette cedex

*lucile.beck@cea.fr

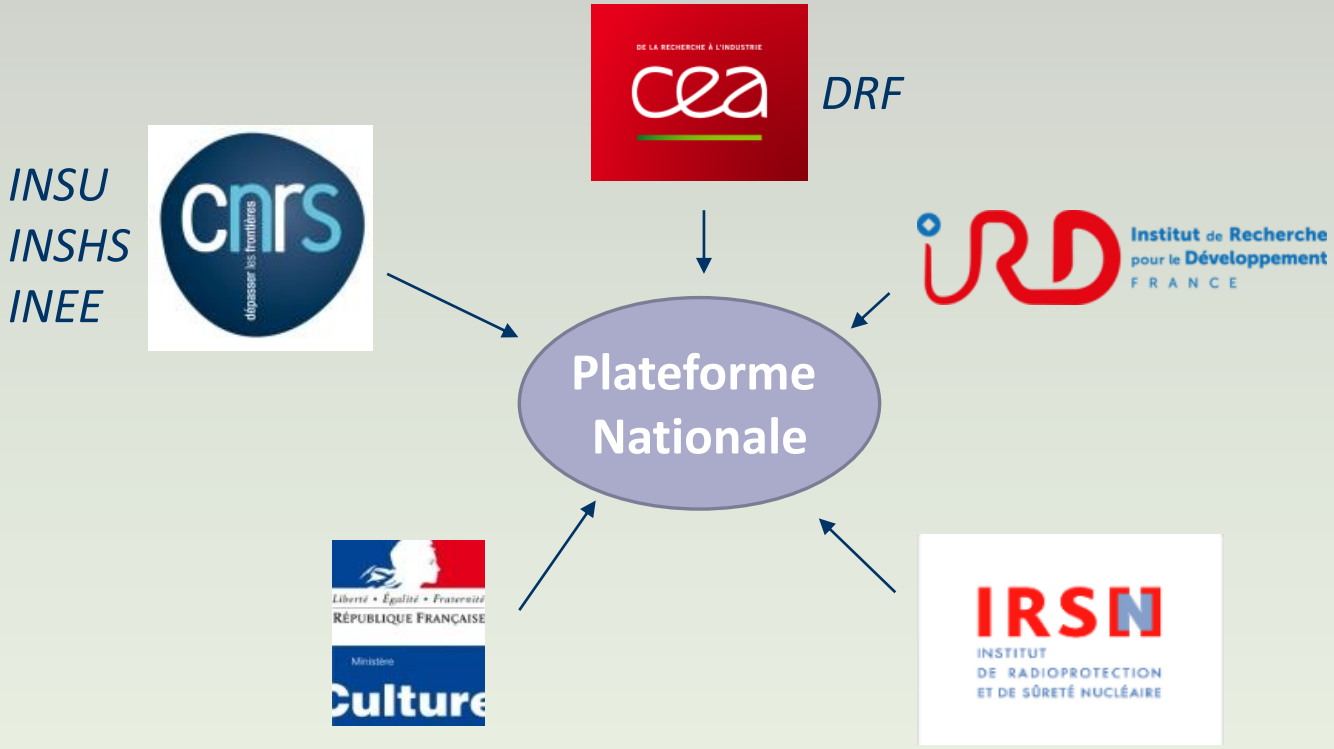
Plan



- Présentation générale du Laboratoire de mesure du carbone 14
- Principe de la méthode de datation par le ^{14}C
- SMA
- Quelques exemples

Le LMC14 : Plateforme Nationale

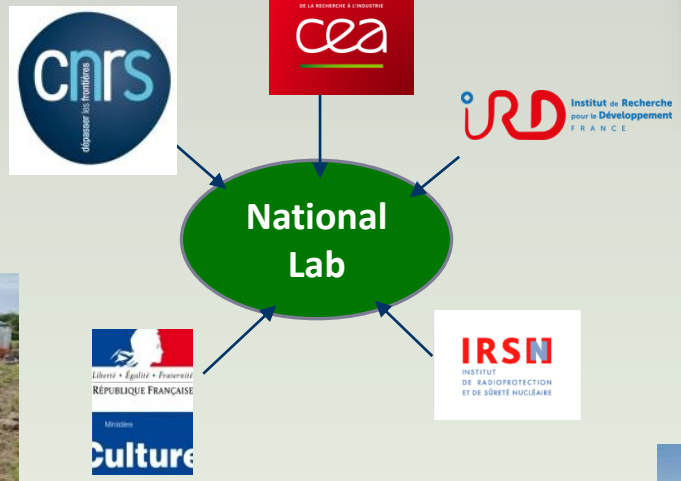
5 partenaires liés par une convention de partenariat depuis 2001 pour l'utilisation en commun du spectromètre de masse par accélérateur ARTEMIS - Plateforme Nationale LMC14



- Historiquement, unité mixte de service N° 2572 créée en 2003, intitulée « Laboratoire de Mesure du Carbone 14 ». Depuis 2015, **Plateforme Nationale LMC14** » rattachée au **LSCE** (Laboratoire des sciences du climat et de l'environnement)

Activités

Service (80 %) : mesurer le carbone 14 de 4000 éch/an



Recherche- (20 %) : 500 éch/an

- <u>Environnement/Environment</u>

Circulation des eaux dans les rivières et deltas: Water circulation in rivers

- <u>Art et Archéologie/Art & archaeology</u>

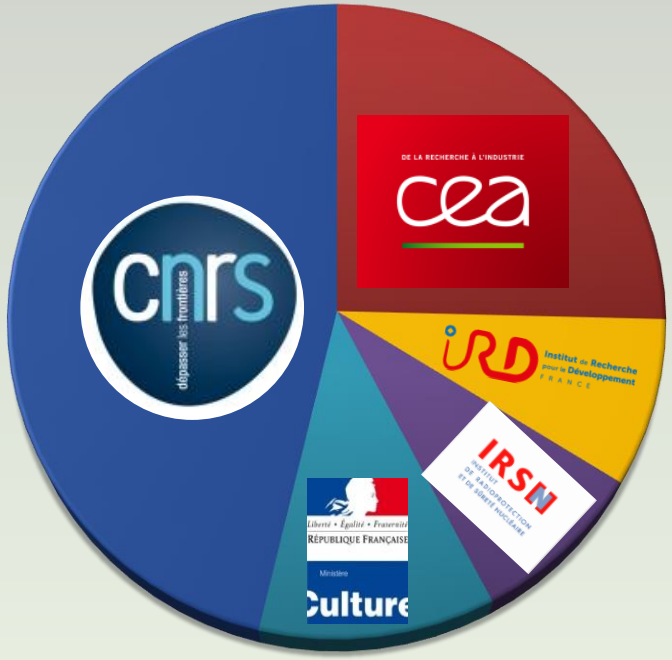
Grottes ornées/ Decorated caves
Chronologie ancienne Égypte/ Ancien Egypt chronology
Fer des cathédrales (ND)/Iron in cathedrals
Musées-restaurateurs/Museums-curators

- <u>Développement analyt./ Analytical dev.</u>

Nouveaux mtx/new materials
µ-échantillons/µsamples

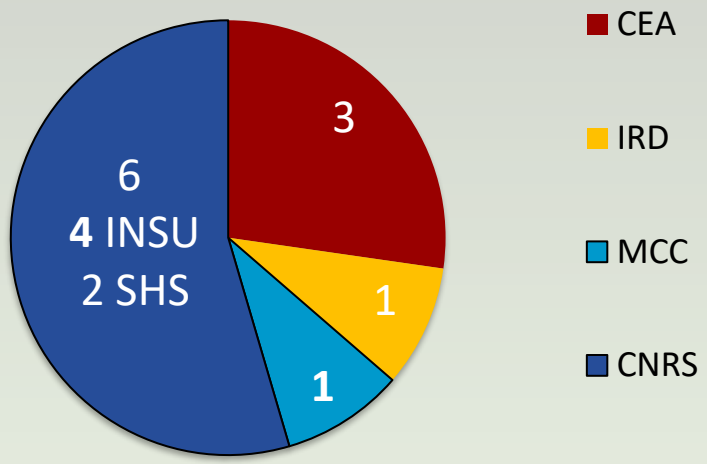
Plateforme Nationale- National laboratory

- 2800 échantillons par an pour 5 organismes → 4000-4500 mesures



70 000 échantillons mesurés depuis 2003 !

11 permanents



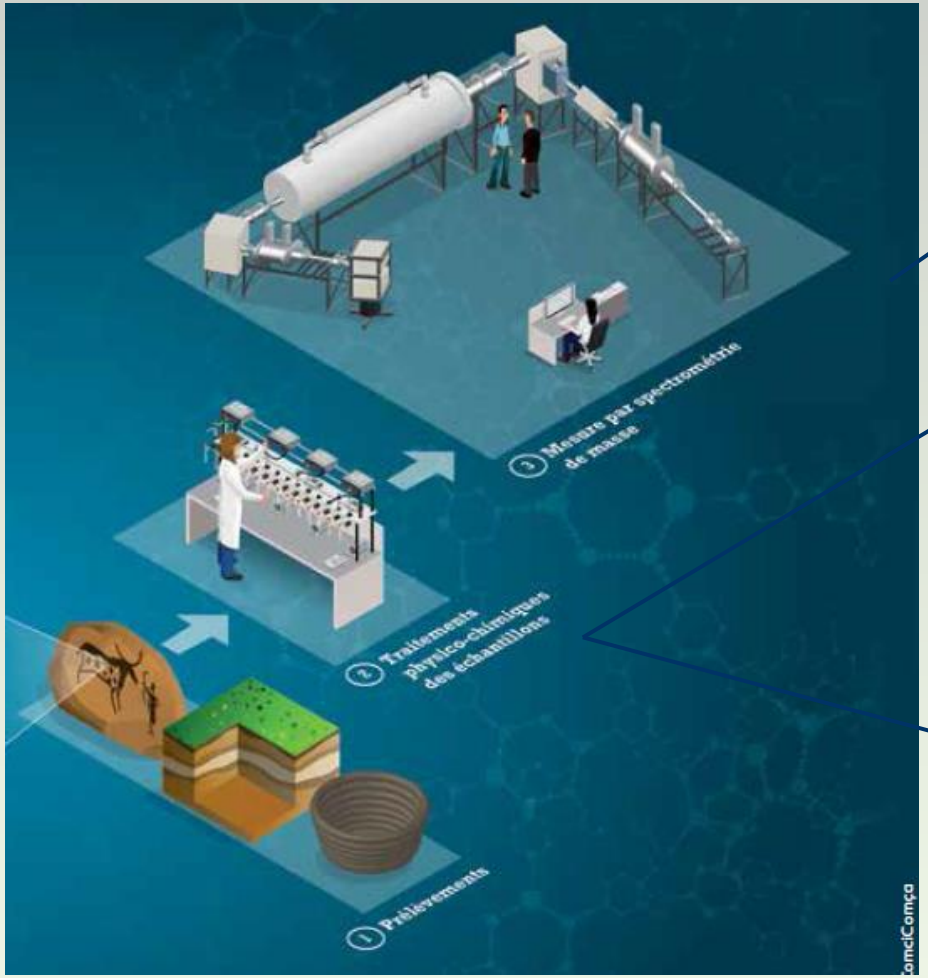
2/3 chimistes -1/3 mesures physiques

4 I-C

6 techniciens ou assitants-ingénieurs

1 gestionnaire

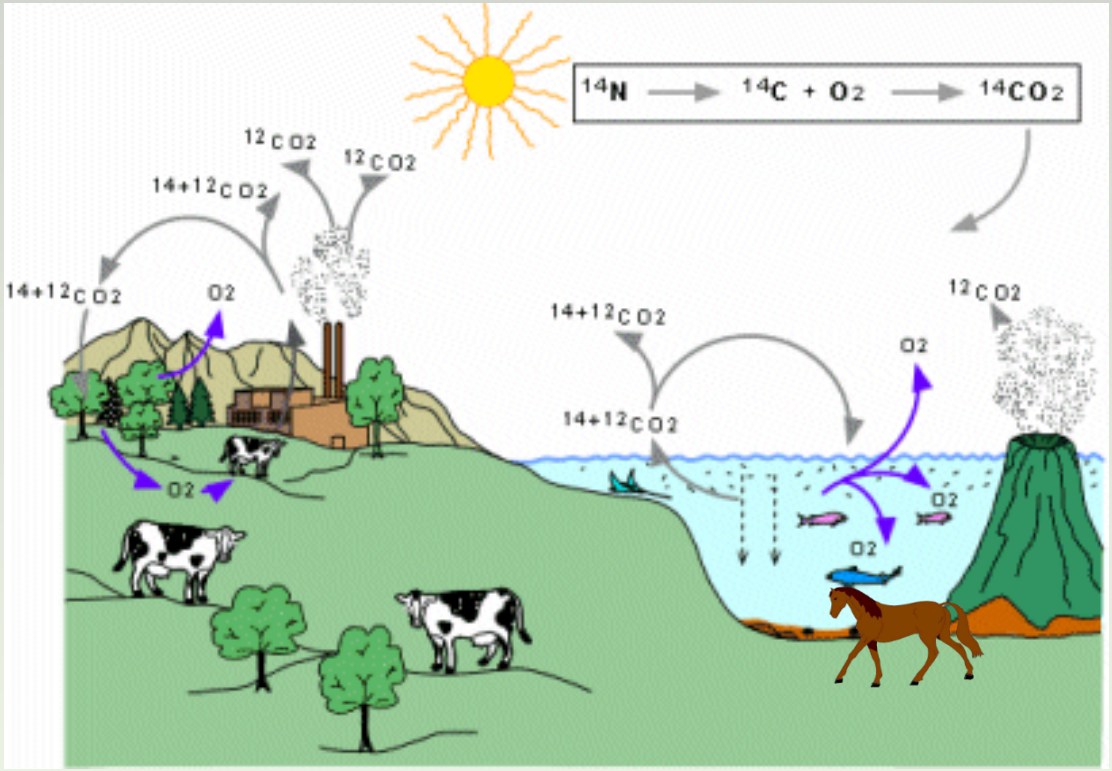
Sur 2 sites du CEA



CEA Saclay

Principe de la datation par le carbone 14

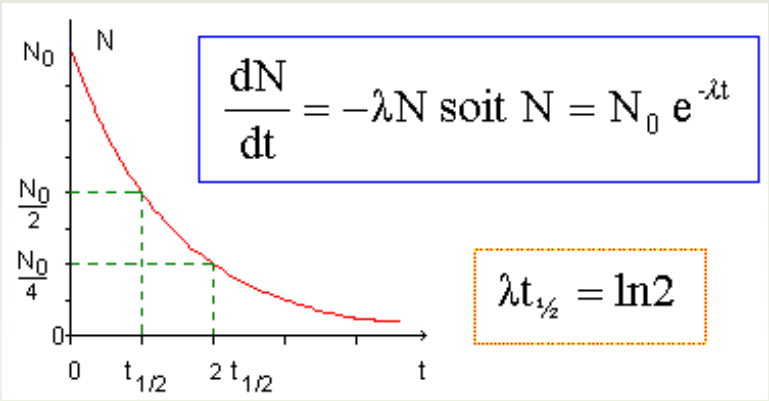
Tout organisme vivant intègre du carbone 14



$t_{1/2}$ = 5730 ans

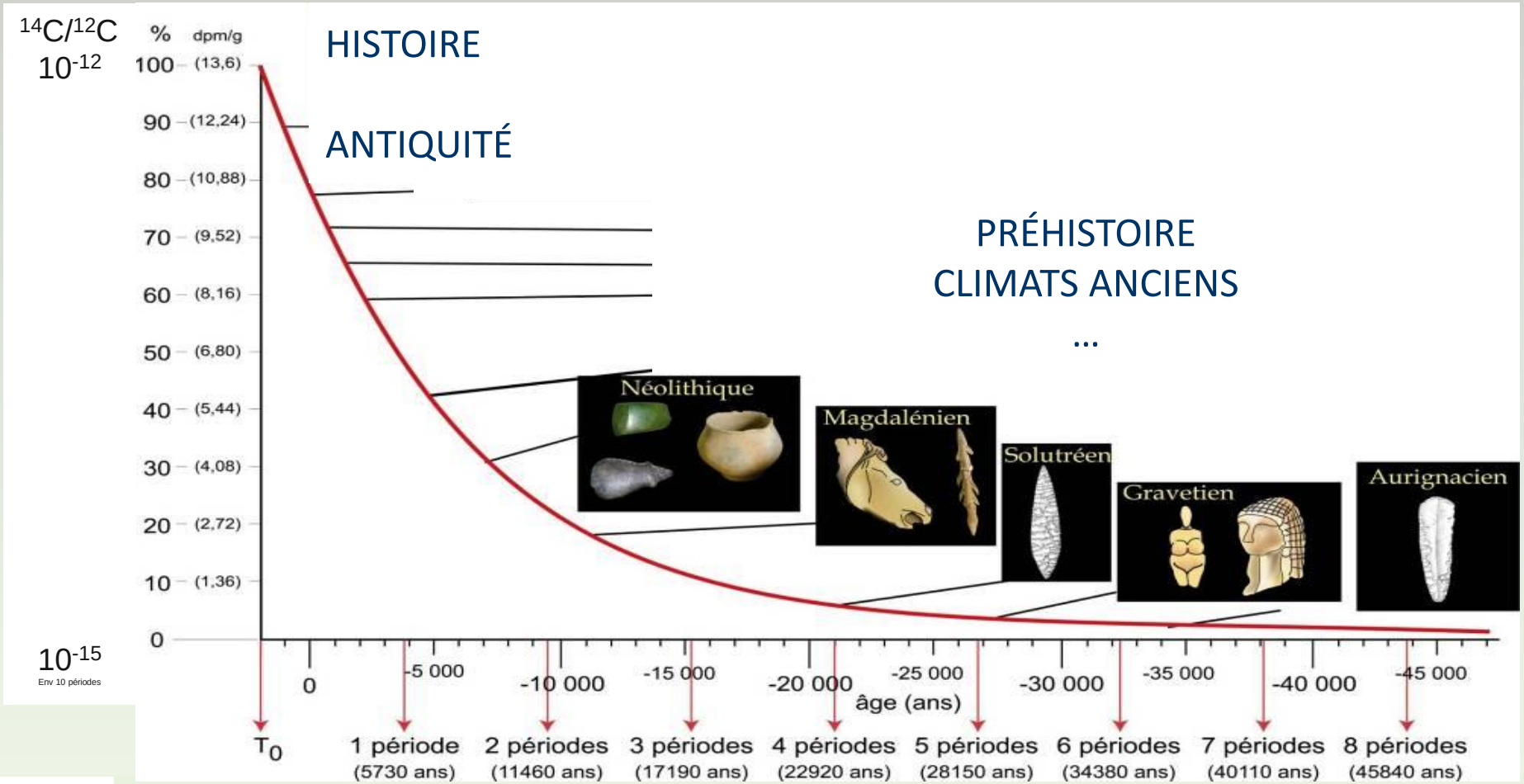
A sa mort, le ^{14}C décroît par désintégration radioactive

$$^{14}_{6}C \rightarrow \beta^- + {}^{14}_{7}N + \nu$$



Jusqu'à 50 000 ans

$$^{14}_{6}C \rightarrow \beta^{-} + ^{14}_{7}N + \nu$$



1946

Libby énonce les principes de la datation au ^{14}C

Prix Nobel de chimie en 1960

Mesure isotopique ou comptage radioactif

$$^{14}_{6}C \rightarrow \beta^{-} + {}^{14}_{7}N + \nu$$

par spectrométrie de masse
par accélérateur (SMA)

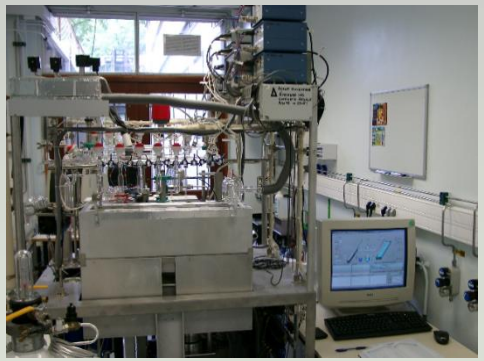
par comptage bêta
par scintillation liquide

Mesure isotopique ou comptage radioactif

Ages absolus en années	Radioactivité spécifique en g par min (dpmg)	% de ^{14}C actif
0	13.56	100
5730	6.78	50
11460	3.39	25
22920	0.84	6.25
40110	0.1	0.78
57300	0.01	0.1

	Comptage β	**AMS**
Charbon de bois	5 à 10 g	5 à 10 mg
Os	100 à 500 g	1 à 5 g
Durée de la mesure	3 jours	1 heure
Précision de la mesure	+/- 40 ans, 5 derniers millénaires +/- 100 ans autour de 10 000 ans +/- 400 ans autour de 30 000 ans	

14C SMA/AMS ARTEMIS au LMC14



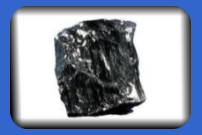
Production

Inspection des échantillons

Prétraitement

Hydrolyse acide pour les carbonates

Combustion pour les échantillons organiques



Collection du CO_2

Pastillage

Graphitisation

$CO_2 + 2H_2$ —Fe à 600°C→ $C+2H_2O$

Mesure SMA

12 échantillons prétraités par jour

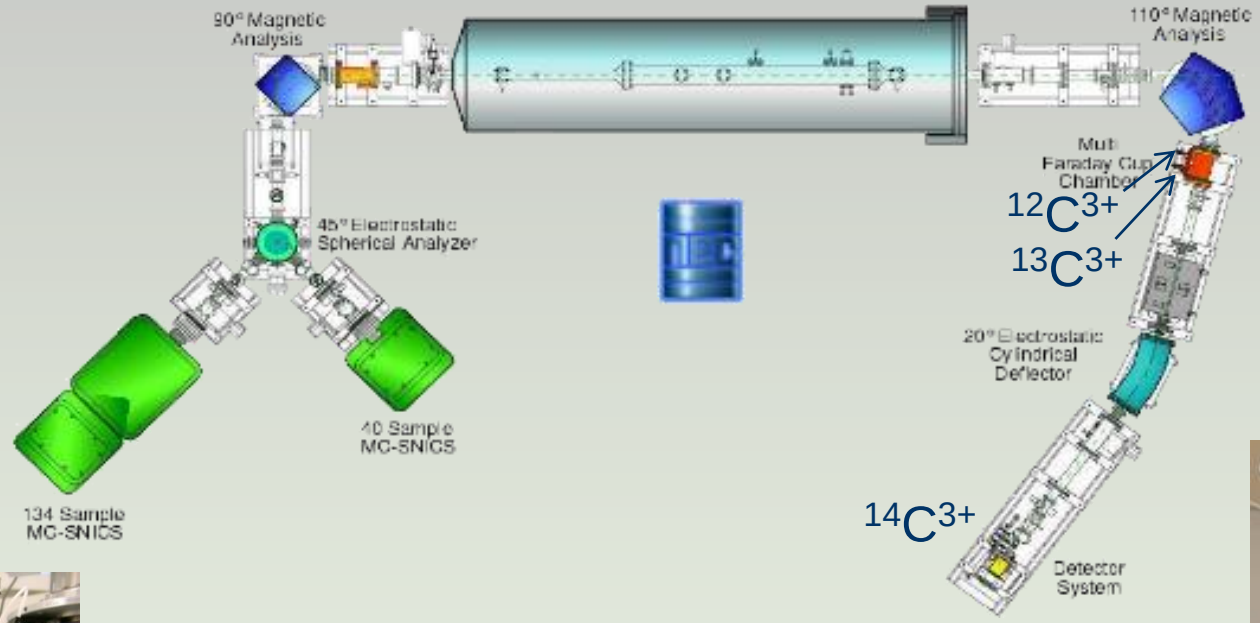
12 ampoules par jour

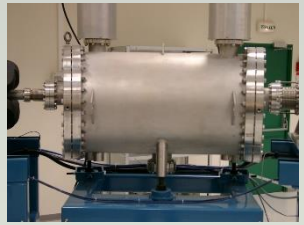
12 ampoules de Lyon et du C2RMF par jour

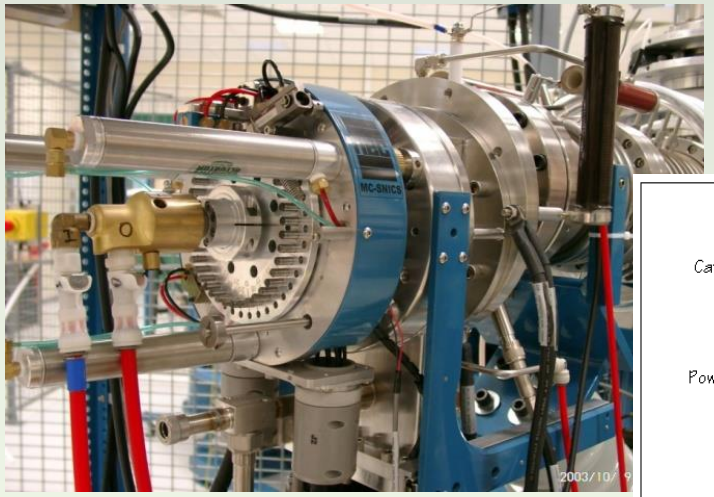
24 cibles de graphite par jour

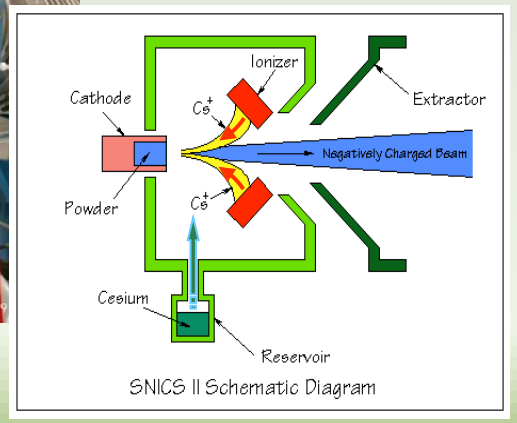
134 dates par semaine
2 à 3 semaines par mois
10-11 mois sur 12

SMA ARTEMIS au LMC14





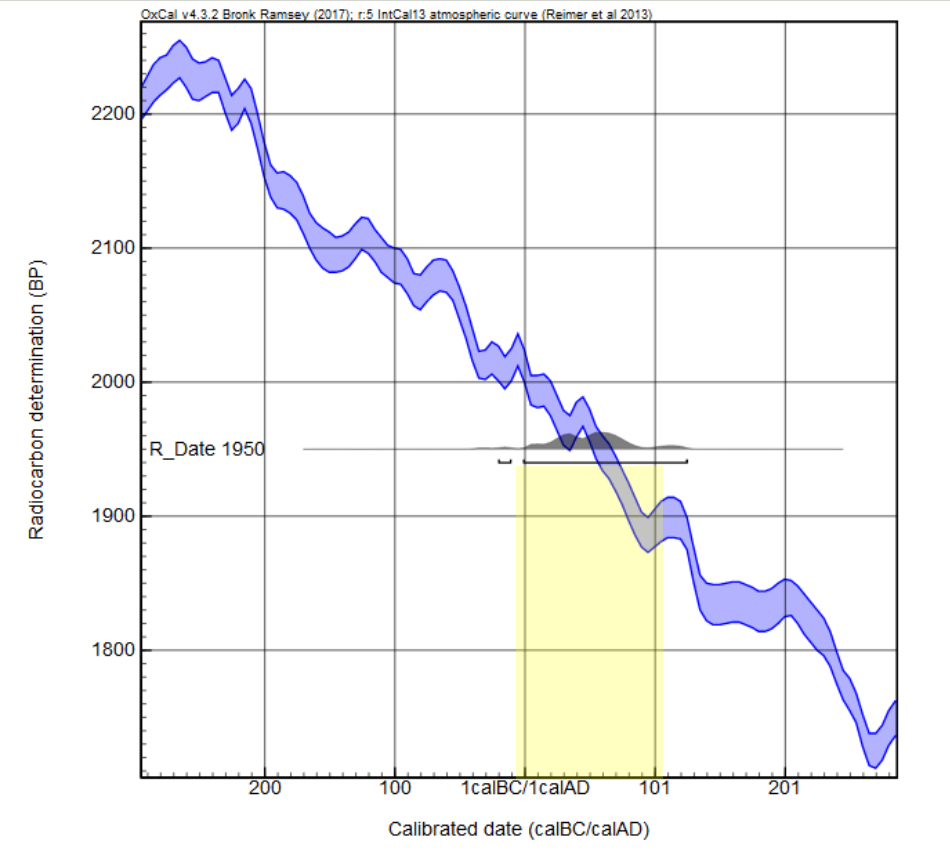




Tandem accelerator

- 3 MV Pelletron tandem (NEC type 9SDH-2)
- Terminal voltage operation : 2.6 MV
- Ar gas stripper (molecules break & charge exchange)
- Final charge states : from 1+ to 4+

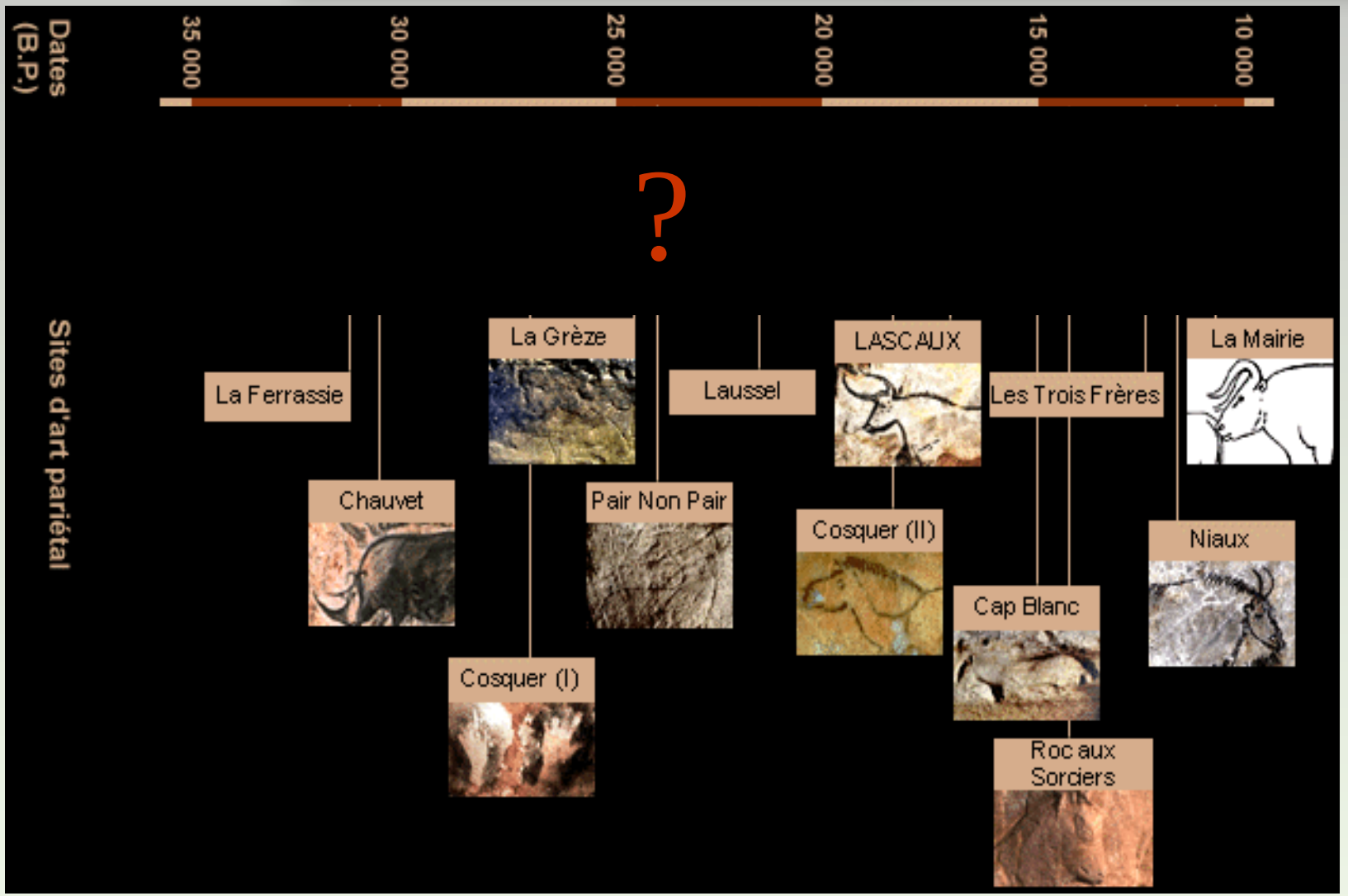
Conversion âge mesuré en date calendaire
Age BP → Date de notre calendrier



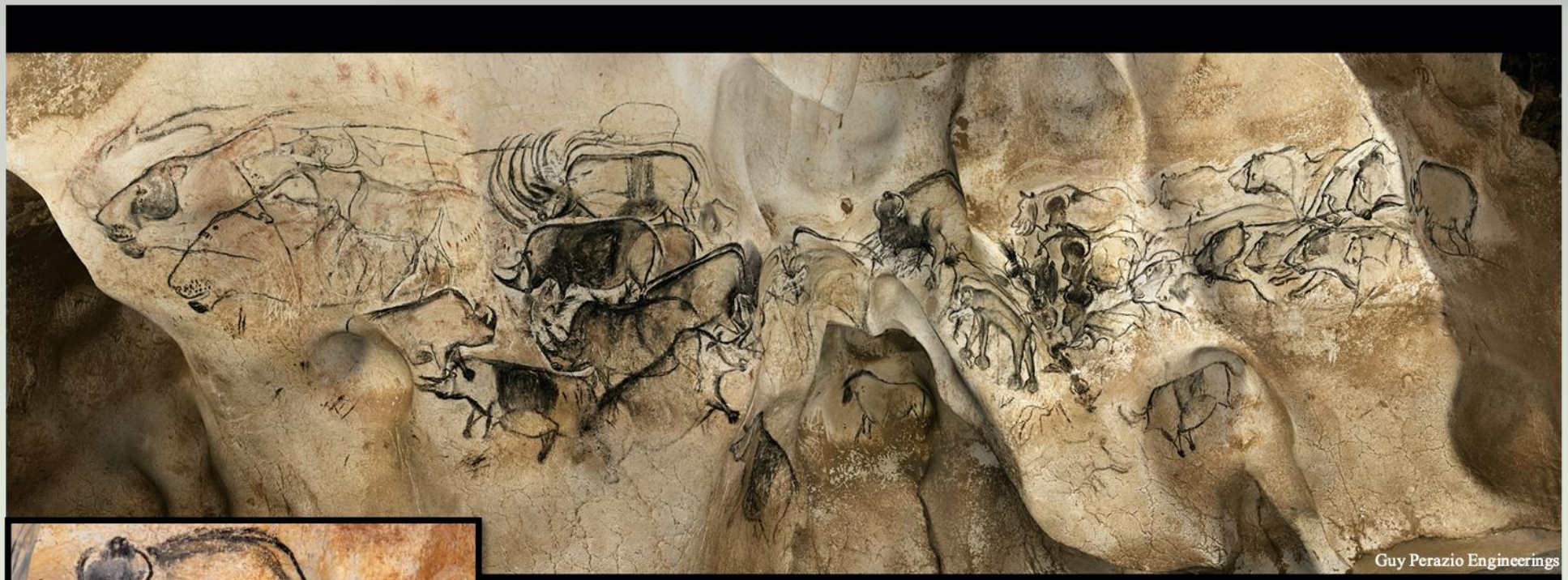
1950 Before Present +/- 30 ans

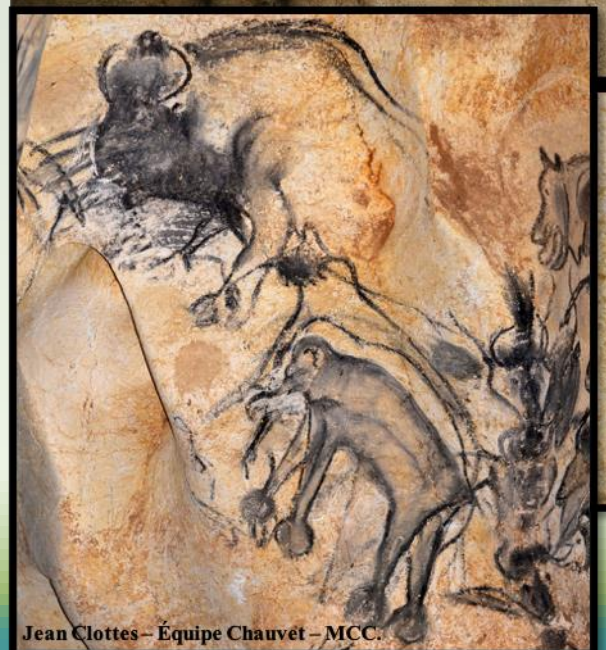
→ 21 av. J.-C. - 125 ap. J.-C.

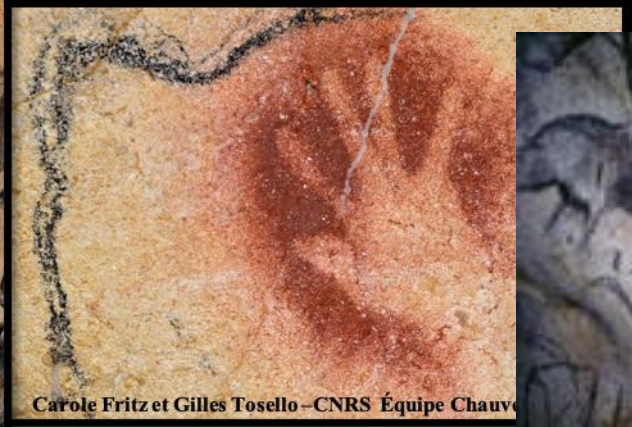
Les grottes ornées



Grotte de Chauvet







Découverte le 18 décembre 1994

Grotte de Chauvet

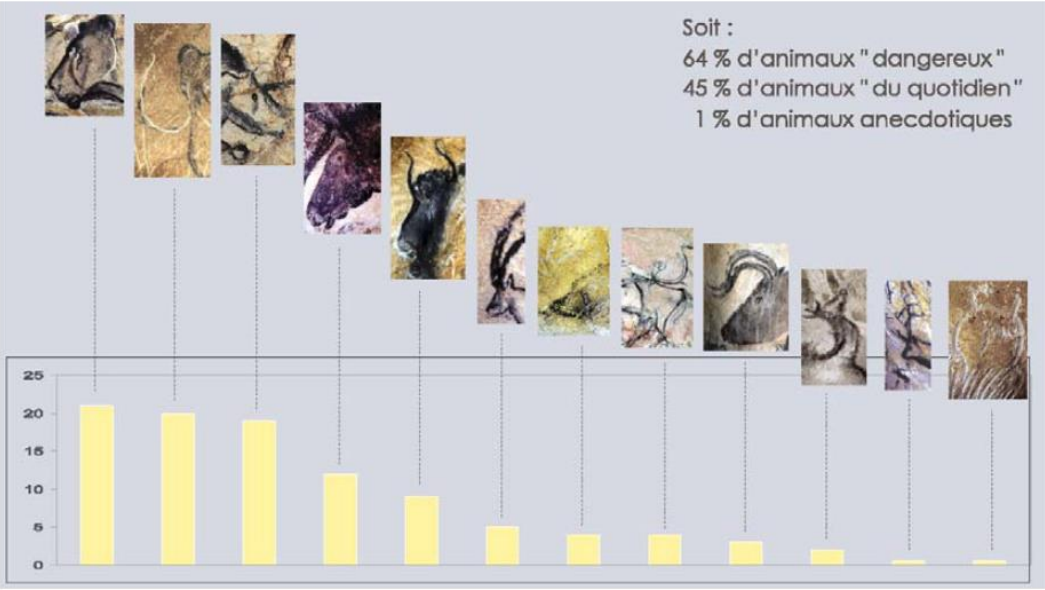


Fig. 3. Diagramme de fréquences des espèces animales constituant le bestiaire de l'ensemble de l'ornementation de la grotte Chauvet.
Fig. 3. Diagram of the animal species frequencies that constitute the bestiary of the entire ornamentation of the Chauvet Cave.

Figures noires au fusain !

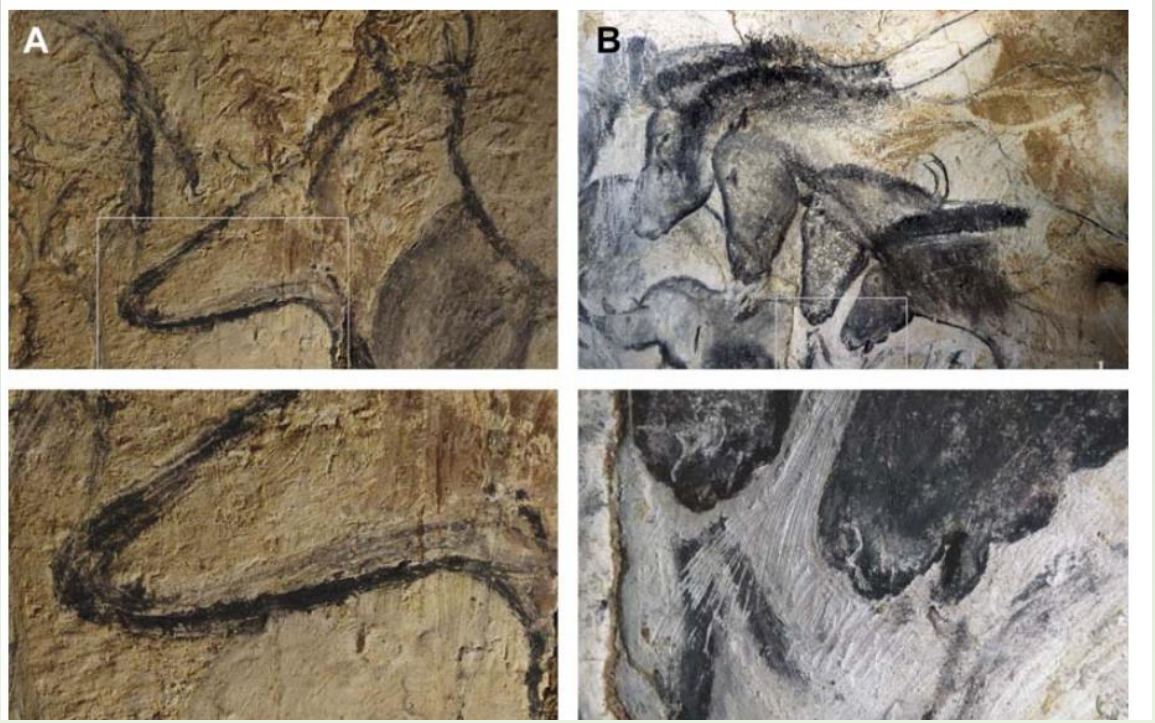


Fig. 4. Exemple de rehauts : (**a**) au fusain, les contours sont d'abord indiqués au trait léger, un remplissage à l'estompe est pratiqué, puis un trait affirmé vient renforcer le contour – panneau des Mégacéros, galerie des Mégacéros (cliché : D. Baffier, V. Feruglio) ; (**b**) au silex, une fois la figure terminée, les contours sont surgravés au silex pour faire ressortir la blancheur du support et donner plus de présence à l'ensemble – panneau des Chevaux (cliché : C. Fritz, G. Tosello).
Fig. 4. Example of enhancements: (**a**) with a charcoal, the contours are first indicated with a light line, a fill up by stumping is then done, then a strong line comes to enforce the contour – Megaloceros Panel, Megaloceros Gallery (© D. Baffier, V. Feruglio), (**b**) with a flint, once the figure is ended, the outlines are engraved with a flint in order to make the whiteness of the wall come out and in order to give more presence to the entire scene – Horses Panel (© C. Fritz, G. Tosello).

Grotte de Chauvet

brief communications

emissions is not justified.

Giulio A. De Leo*, Luca Rizzi†, Andrea Caizzi†, Marino Gatto§
*Dipartimento di Scienze Ambientali, Università degli Studi di Parma, Parco Area delle Scienze, Parma 43100, Italy
e-mail:deleo@dsa.unipr.it
†Centro Elettronecnico Sperimentale Italiano, Business Unit Ambiente, Via Reggio Emilia 39, Segrate 20090, Italy
§Centro di Ingegneria Biomedica, Consiglio Nazionale delle Ricerche, Politecnico di Milano, Piazza Leonardo da Vinci 32, Milano 20133, Italy

1. Remarks by President G. W. Bush on Global Climate Change (Office of the Press Secretary, The White House, 11 June 2001).
2. De Leo, G. A., Rizzi, L. & Caizzi, A. in Proc. 29th Int. Conf. Automation and Decision Making 247–256 (IASTED, Milan, 2000).
3. Callan, S. J. & Thomas, J. M. Environmental Economics and Management: Theory, Policy and Applications (Irwin, Chicago, 1996).
4. De Paoli, L. & Lorenzoni, A. Economia e politica delle fonti rinnovabili e della cogenerazione (Franco Angeli, Milan, 1999).
5. IEA/OECD Experience Curves for Energy Technology Policy (IEA, Paris, 2000) (http://www.iea.org/public/studies/curves.htm).
6. European Commission Externe: Externalities of Energy Vols 1–6 (EC, Brussels, 1995) (http://externe.jrc.es/index.html).
7. Rowe, R. D. et al. ESEERCO, New York State Environmental Externalities Cost Study Vols 1, 2 (Oceana, New York, 1995).
8. Russell, L. (ed.) External Costs and Benefits of Fuel Cycles (Oak Ridge National Laboratory and Resources for the Future, Oak Ridge, Tennessee, 1994).
9. Gatto, M. & De Leo, G. A. Bioscience 50, 367–375 (2000).
10. Interlaboratory Working Group Scenarios for a Clean Energy Future (Oak Ridge National Laboratory, Tennessee, and Lawrence Berkeley National Laboratory, California, ORNL/CON-476 and LBNL-44029, 2000).

Supplementary information is available at http://www.nature.com or as paper copy from the London editorial office of Nature.

Palaeolithic paintings

Evolution of prehistoric cave art

Sophisticated examples of European palaeolithic parietal art can be seen in the caves of Altamira, Lascaux and Niaux near the Pyrenees, which date to the Magdalenian period (12,000–17,000 years ago), but paintings of comparable skill and complexity were created much earlier[1,2], some possibly more than 30,000 years ago[3]. We have derived new radiocarbon dates for the drawings that decorate the Chauvet cave in Vallon-Pont-d'Arc, Ardèche, France, which confirm that even 30,000 years ago Aurignacian artists, already known as accomplished carvers[3], could create masterpieces comparable to the best Magdalenian art[4]. Prehistorians, who have traditionally interpreted the evolution of prehistoric art as a steady progression from simple to more complex representations, may have to reconsider existing theories of the origins of art.

The chronology of European prehistoric cave paintings has been loosely based on the style of fauna depicted or on dated remains left by cave occupants, but has become more precise with radiocarbon dating of the charcoal pigments themselves. Accelerator mass spectrometry, which relies on the separation and counting of carbon isotopes, requires much less of this precious sample material than traditional ^{14}C-dating techniques.

Uncalibrated radiocarbon ages in excess of 22,000 years (22 Kyr before present (BP)) have been calculated for paintings in several French caves, mostly on the tandem accelerator at Gif-sur-Yvette, France[5]. The charcoal of the painting itself can be dated[6], either directly or in trace organic residues that have a temporal relationship to the paintings, for example as charcoal mingled with ochre pigments. Also datable are smudges left by torch-bearers which, if found on the calcite coating of a drawing, indicate a time before which the drawing must have been created.

Indirect evidence of extensive painting activity before the Solutrean period comes from radiocarbon dates for drawings at two French caves — a 26.9-Kyr-old bone chip was extracted from a fissure crossing a stencilled hand at Gargas[7], and three burnt bones, mixed with red and yellow ochre at the base of several designs in the Grande Grotte at Arcy-sur-Cure[8], are aged at 26–28 Kyr; torch smears marring the red frieze date to about 27 Kyr BP[9].

At four other French caves, charcoal from the drawings themselves has been dated. During investigations at Cougnac, dates between 23 and 25 Kyr BP were obtained for two giant deer[3,10], and at nearby Pech Merle, the right-facing spotted horse is dated to 24.7 Kyr BP[3]. In Cosquer, we dated 13 drawings[3,11] at 27–28 Kyr BP for two stencilled hands, a bison and an oval sign — all other drawings but two were 18–20 Kyr old (cave-floor charcoal fits within the same two periods[3]).

In the Chauvet caves, which consist of several chambers, we derived radiocarbon dates of between 29.7 and 32.4 Kyr BP for charcoal (0.27–1.40 mg carbon) from animals painted in the Salle du Fond and in the 'horse' panel (Fig. 1) of the Hillaire chamber[4]. Two torch rubbings, one from the same panel and another from the Cierge chamber, were about 27 Kyr old, a reasonable age considering that in one case the torch was scraped against a calcite-coated animal. We obtained an age of 31.4 Kyr for a giant deer at the entrance to the Megaceros gallery (see supplementary information). Charcoal was obtained from under a bear skull placed on a stone slab in the Crâne chamber and from the Megaceros gallery, which is carpeted with charcoal particles of various sizes as though it had been used as a charcoal factory[4]. Apart from two roughly 26-Kyr-old specimens, most of the charcoal was produced between 29 and 32 Kyr BP, suggesting that there may have been two significant episodes of human intrusion before the cave was sealed off by a rockfall.

This latest comprehensive dating confirms our earlier provisional assignment of the Chauvet cave art to the Aurignacian period[3]. Future discoveries will reveal the nature of paintings that predate those in the Chauvet cave.

H. Valladas*, J. Clottes†, J.-M. Geneste‡, M. A. García§, M. Arnold¶, H. Cachier*, N. Tisnérat-Laborde*
*Laboratoire des Sciences du Climat et de l'Environnement, UMR CEA-CNRS 1572, 91198 Gif-sur-Yvette Cedex, France
e-mail: helene.valladas@lsce.cnrs-gif.fr
†11 Rue du Fourcat, 09000 Foix, France
‡Service Régional de l'Archéologie d'Aquitaine, DR AC d'Aquitaine, 54 Rue Magendie, 33074 Bordeaux, France
§Maison de l'Archéologie et de l'Ethnologie, 21 Allée de l'Université, 92023 Nanterre, France
¶UMS 2004 (CNRS-CEA), Tandétron Bâtiment 30, 91198 Gif-sur-Yvette, France

1. Leroi-Gourhan, M. Les Grottes Ornées de la Préhistoire (Erasme, Paris, 1995).
2. Clottes, J. & Courtin, J. La Grotte Cosquer (Seuil, Paris, 1994).
3. Clottes, J. et al. C. R. Acad. Sci. Paris 320, 1133–1140 (1995).
4. Clottes, J. (ed.) La Grotte Chauvet: L'art des Origines (Seuil, Paris, 2001).
5. Valladas, H. et al. Radiocarbon (in the press).
6. Valladas, H. et al. Nature 357, 68–70 (1992).
7. Clottes, J. & Valladas, H. Bull. Soc. Préhist. Fr. 89, 259–274 (1992).
8. Girard, M. et al. Cahiers Archéologiques de Bourgogne 6, 17–23 (1996).
9. Baffier, D. et al. Int. Newslett. Rock Art 28, 1–3 (2001).
10. Valladas, H., Cachier, H. & Arnold, M. Rock Art Res. 7, 18–19 (1990).
11. Clottes, J. et al. Bull. Soc. Préhist. Fr. 89, 259–274 (1992).

Supplementary information is available at http://www.nature.com or as paper copy from the London editorial office of Nature.

© 2001 Macmillan Magazines Ltd

In the Chauvet caves, which consist of several chambers, we derived radiocarbon dates of between 29.7 and 32.4 Kyr BP for charcoal (0.27–1.40 mg carbon) from animals painted in the Salle du Fond and in the 'horse' panel (Fig. 1) of the Hillaire chamber[4]. Two torch rubbings, one from the same panel and another from the Cierge chamber, were about 27 Kyr old, a

- 2004 : First Intercomparison Program, 6 ^{14}C laboratories.

Successful results: average age of ~32 ka BP for the three pieces of charcoal collected from one archaeological hearth structure in the Galerie des Mégacéros (Cuzange et al. 2007)

- 2012 : Second Intercomparison Program, 10 ^{14}C laboratories. *(Quiles et al. 2014).*

Grotte de Chauvet

Quiles et al. Radiocarbon 56, 2014

Figure 1 Archaeological hearth structures in the Galerie des Mégacéros, from which GC-12-01 (a) and GC-12-04, GC-40, GC-41, and GC-42 (b) were sampled. ©Centre National de la Préhistoire, France, 2013.

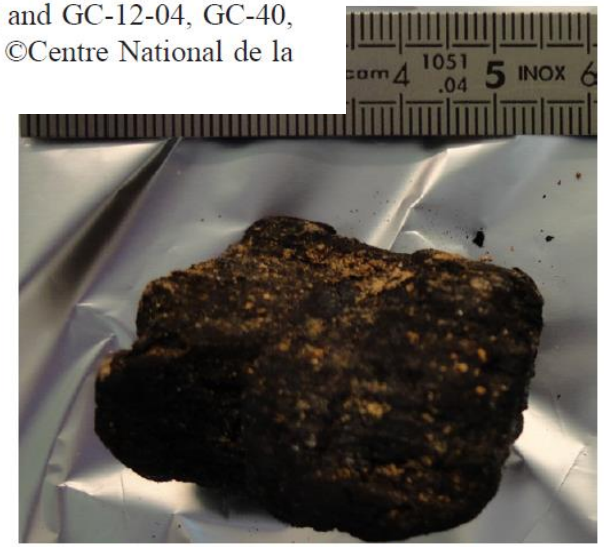


Figure 2 Sample GC-12-04 lifted from an archaeological hearth structure in the Galerie des Mégacéros. ©Laboratoire des Sciences du Climat et de l'Environnement, France, 2012.

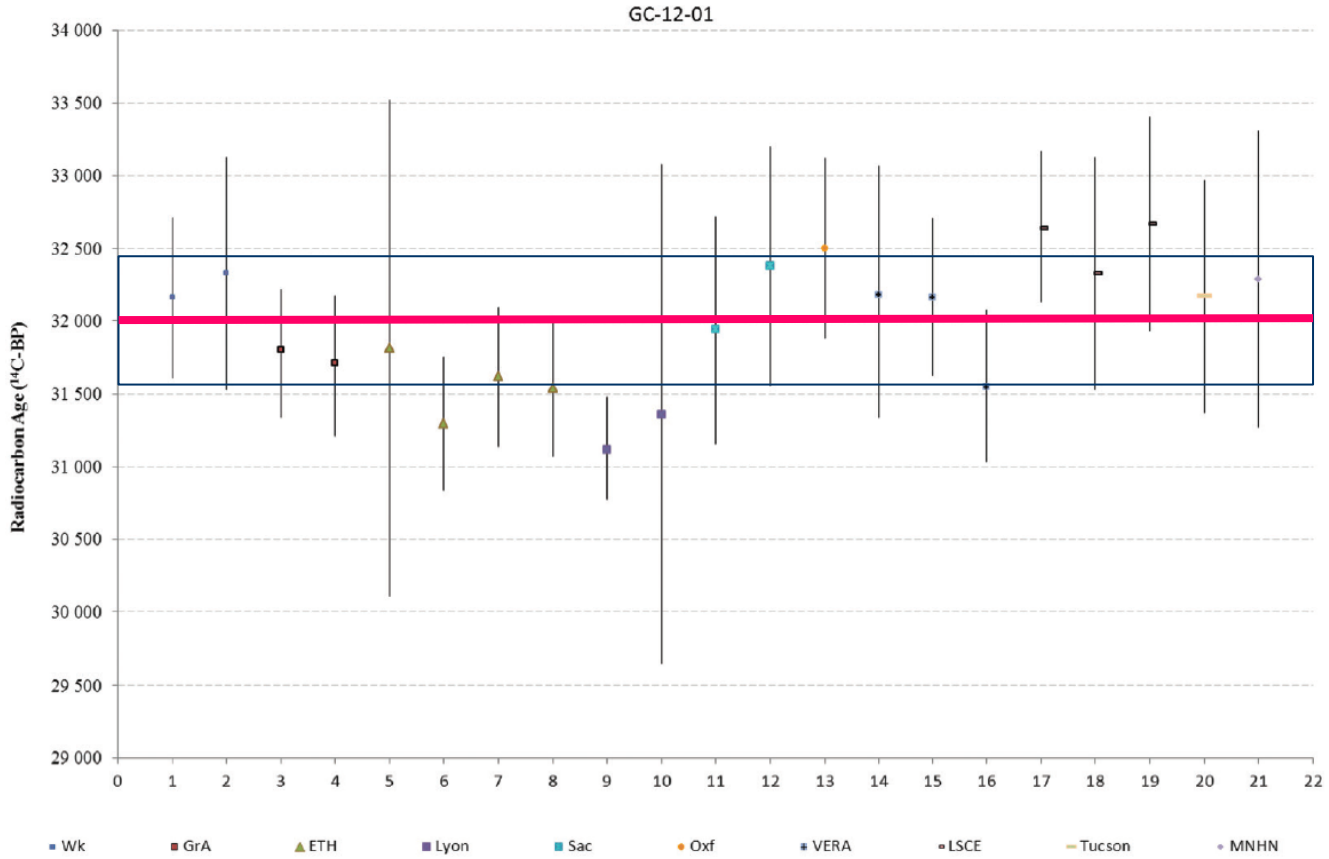
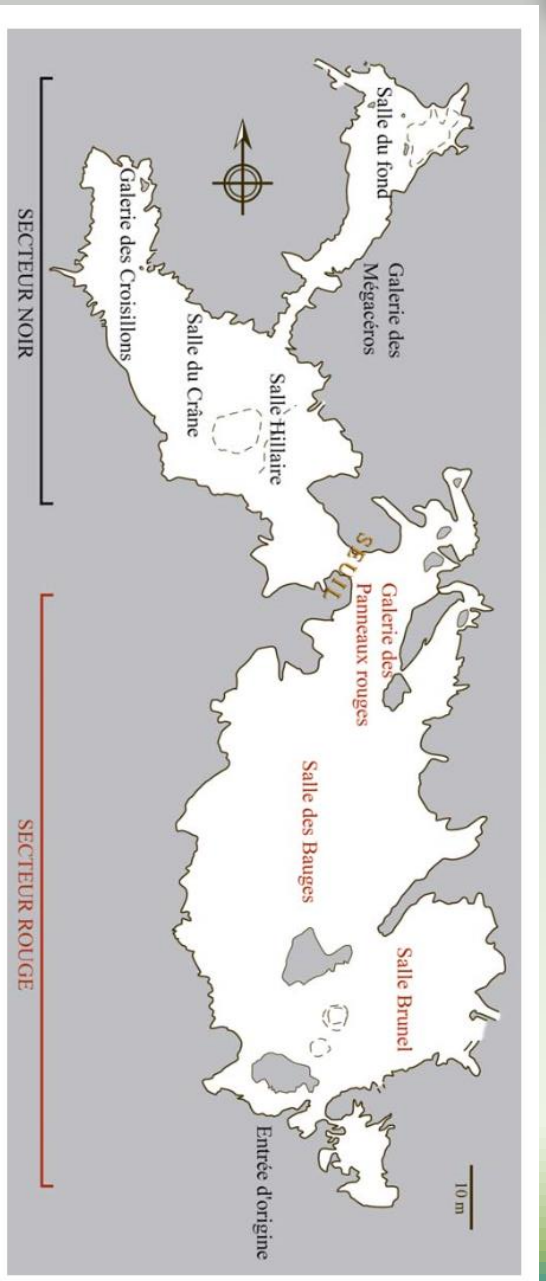


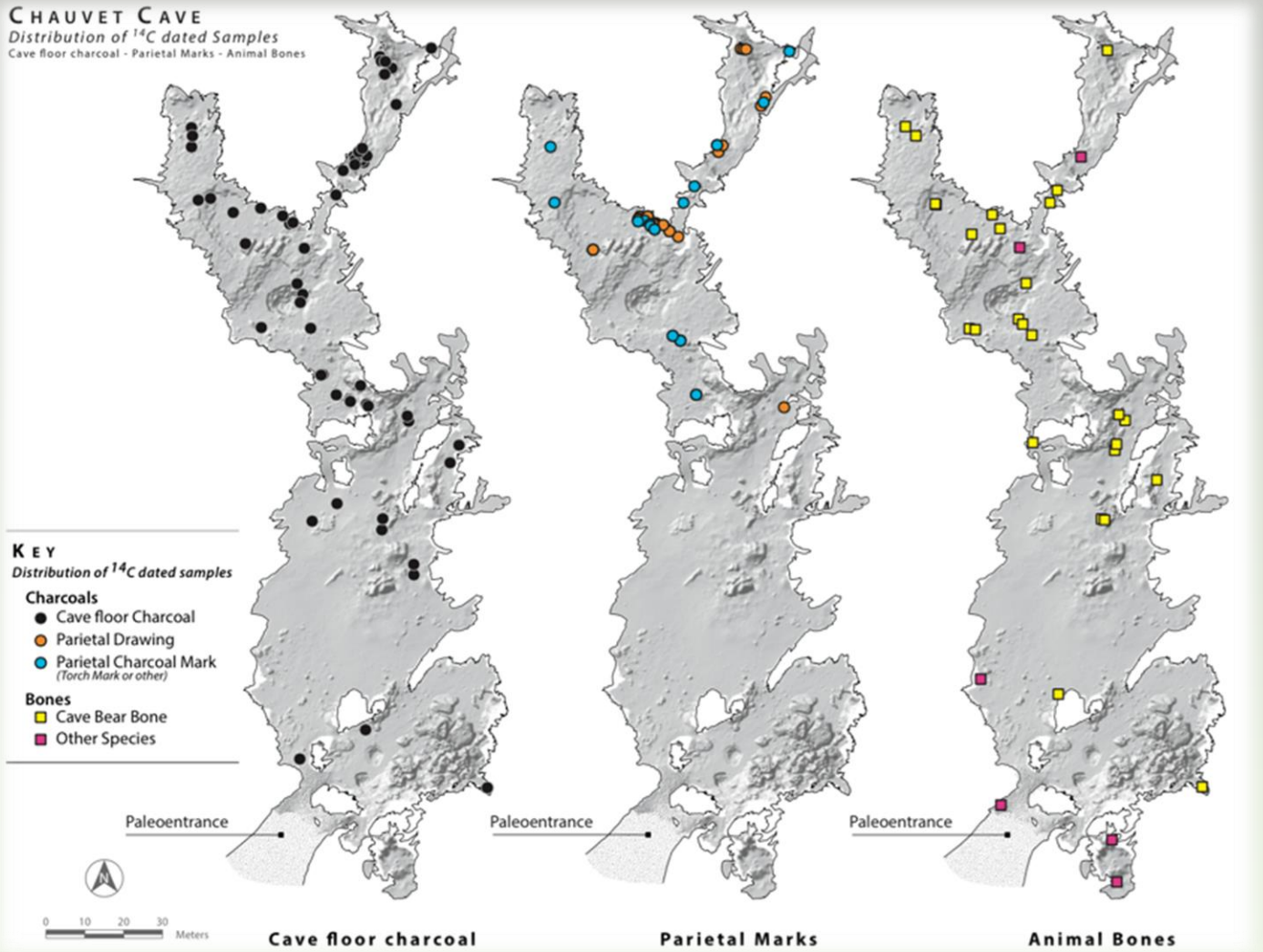
Figure 3 Radiocarbon results obtained for GC-12-01, with a 2σ range. The 10 laboratories performed 21 measurements, using their own chemical pretreatment (ABA, ABOX, "mild acid only," alkaline fraction) and AMS facility (seven different ones). They range from 32,670 ± 380 to 31,120 ± 180/170 BP with an average value of 31,979 ± 378 BP; all are compatible with a 2σ range. Note that the large uncertainly of one ETH analysis is due to the small amount of C used (see text).

LSCE

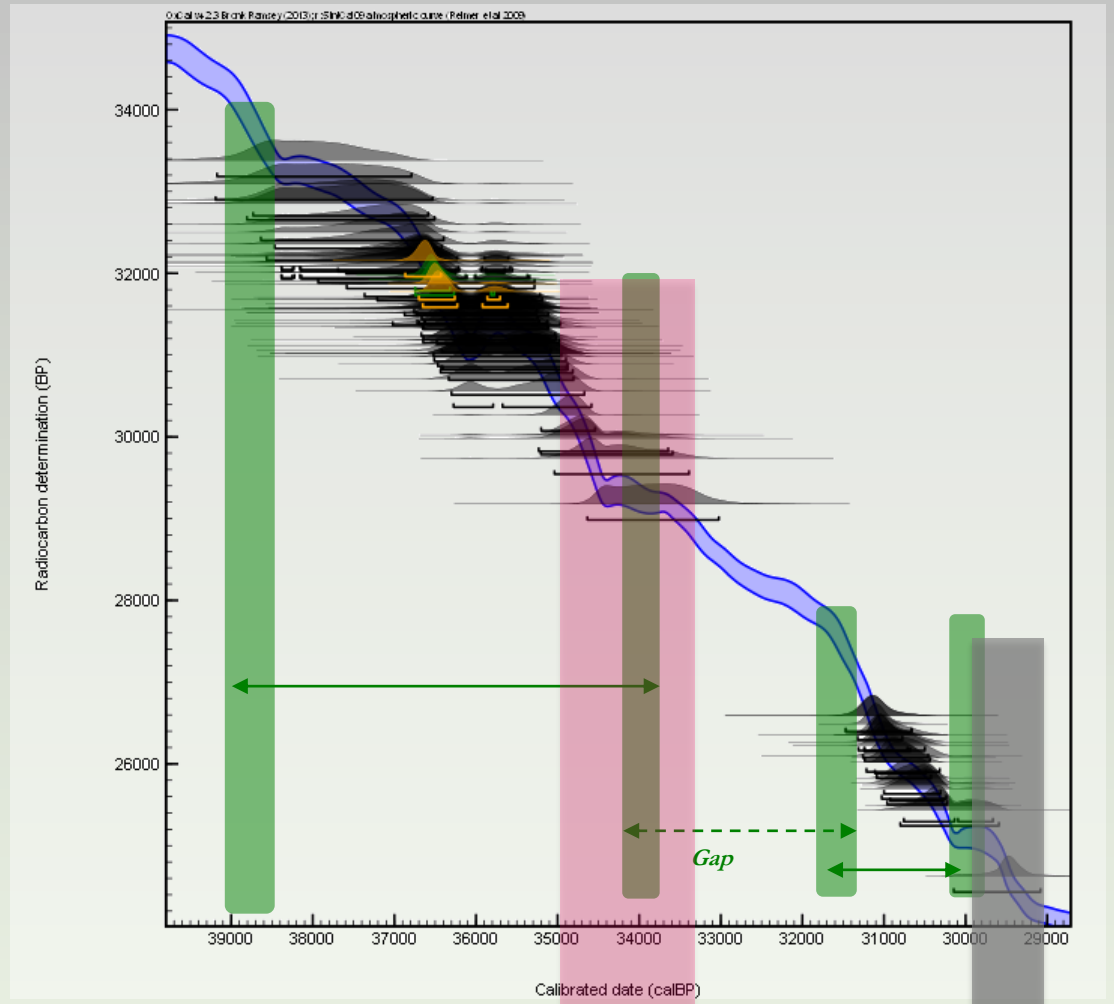
Grotte de Chauvet : la compil

- Jeu de plus de 230 datations





71 → 159 dates | 42 | 36



^{36}Cl :
fermeture de la grotte

Sadier et al., 2012, PNAS 109 (21)

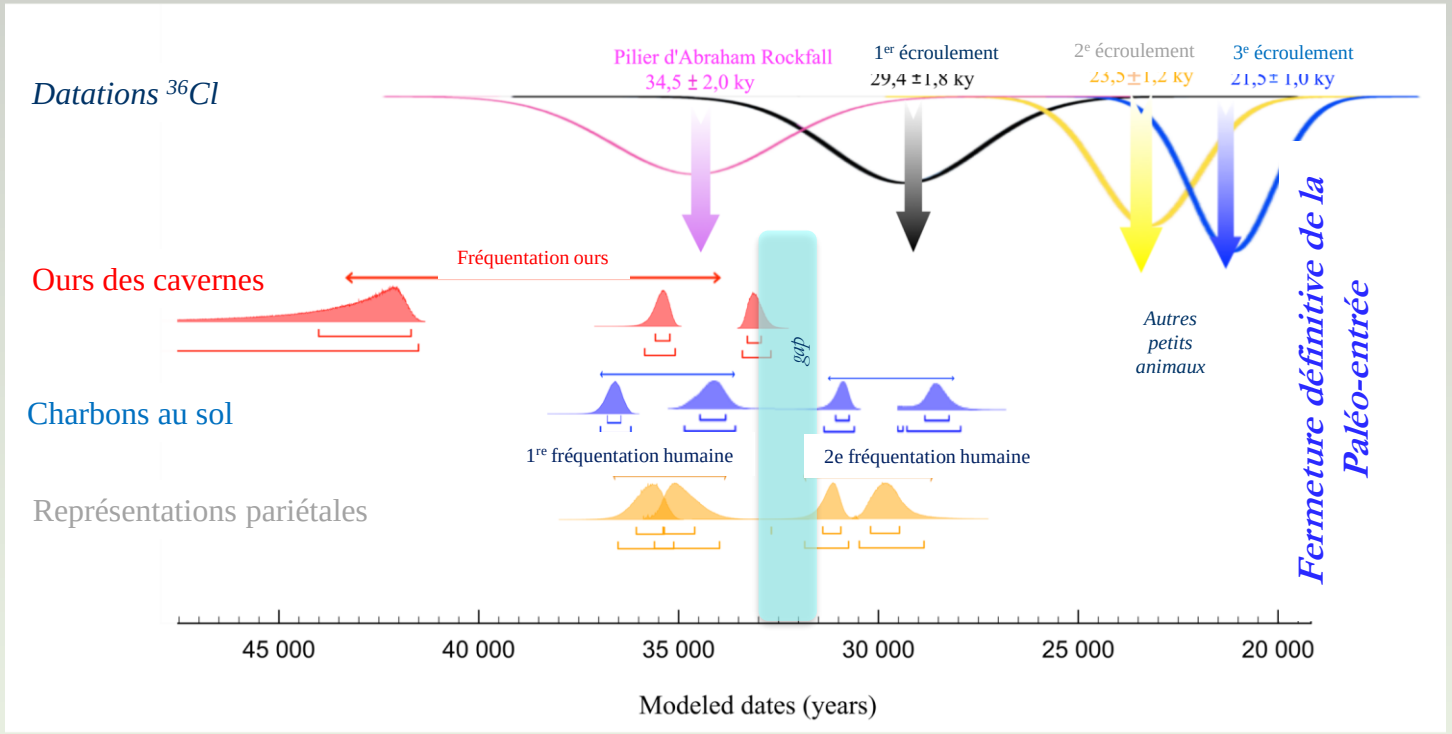
E0 : Pilier d'Abraham
34.5 ± 2.0 kans

E1
29.4 ± 1.8 kans

E2
23.5 ± 1.2 kans

E3
21.5 ± 1.0 kans

Les temps de la grotte Chauvet-Pont d'Arc



Quiles et al., *PNAS 113*, 2016

Le blanc de plomb : des cosmétiques antiques à la peinture

Cérusite $PbCO_3$

Garde robe de Marguerite de Bavière

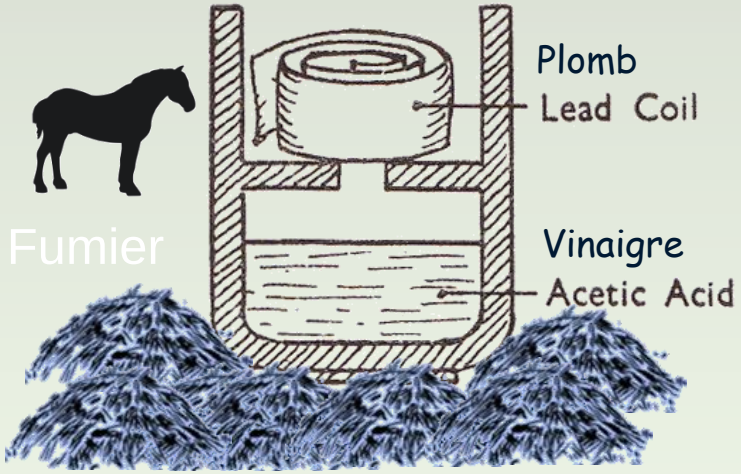
$Pb_2(CO_3).Cl_2$

Walter al., Nature 397, 1999

Lucile Beck-2023

Fabrication des carbonates de plomb historiques

Théophraste (IVe siècle av. J.-C.)
«*Ils sont préparés artificiellement le plomb blanc. Du **plomb** de la grosseur d'une brique est placé dans des récipients sur du **vinaigre** et, lorsque ceci acquiert une masse épaisse, ce qui se fait généralement en dix jours, les bocaux sont ouverts et une sorte de **moisissure** est raclée. La partie raclée est broyée dans un mortier et décantée fréquemment, et ce qui reste finalement au fond est du plomb blanc.* »



PhD M. Stols-Witlox, 2014
Thèse V. Gonzalez, 2016

Figure III. 19: Étapes de la fabrication du blanc de plomb commercial issu d'un procédé d'empilement (a) : rouleaux de plomb métallique, (b) : strate de jarres contenant les rouleaux et prêtes à être recouvertes de fumier, (c) : rouleaux corrodés lors de l'ouverture des jarres après 4 mois de corrosion, (d) : pigment obtenu (on constate que le produit s'est détaché sous forme d'écailles). © Natural Pigments

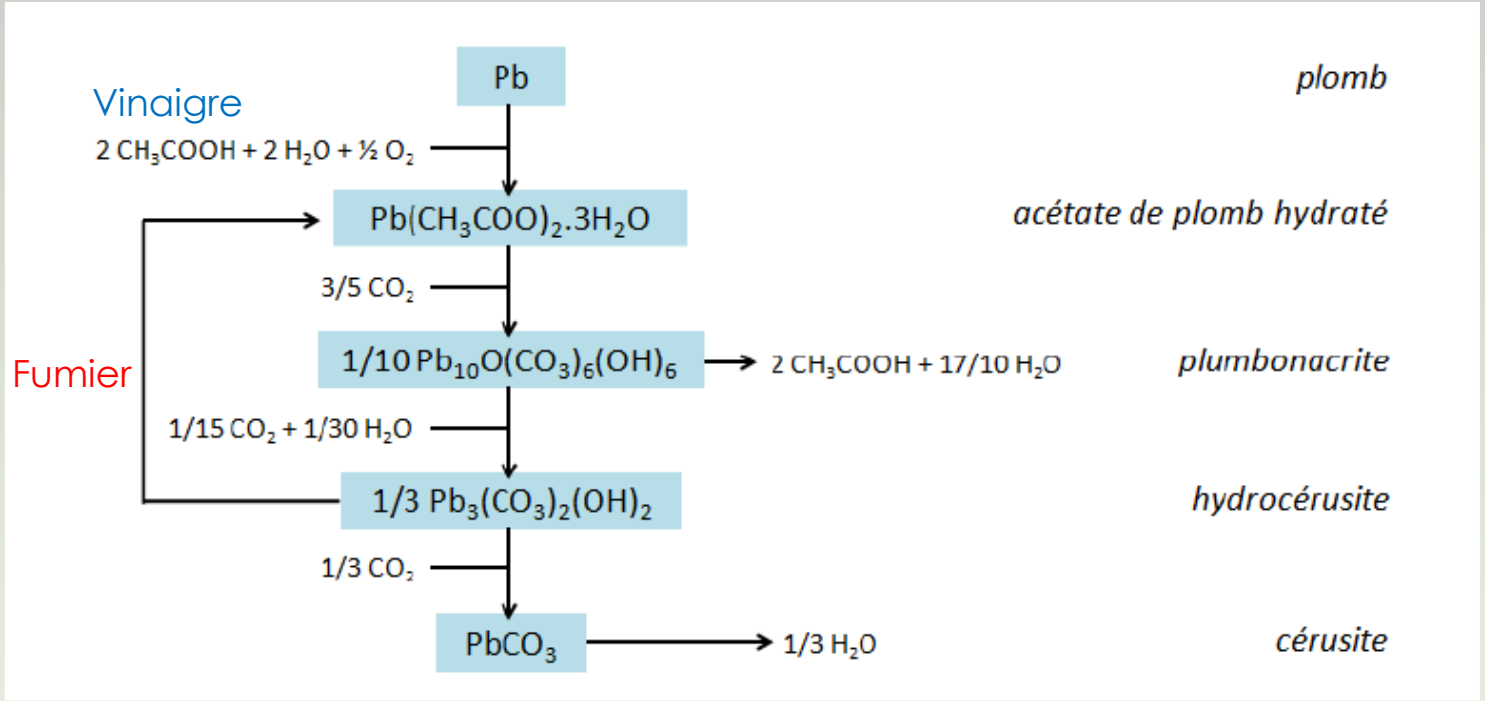
Fabrication des carbonates de plomb historiques et datation carbone 14

Fumier produit du CO_2

Vinaigre

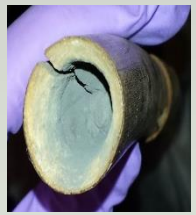
Procédé des loges ou procédé hollandais

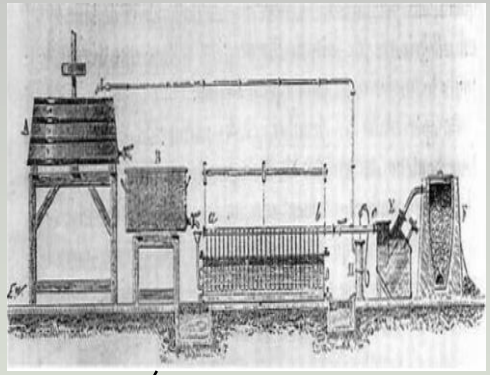
Fumier produit du CO_2



Thèse M. Stols-Witlox (2014)
Thèse V. Gonzalez (2016)
V. Gonzalez, Corrosion Sciences (2019)

Fumier = CO_2 d'origine organique ➔ C d'origine organique ➔ ^{14}C ➔ datation





2000 BC

4th – 3rd century BC

1400

1500

19th

Castle of Germolles, Burgundy

Church of the Cordeliers, Fribourg

Clichy process = wet process

A N T I Q U I T	E M A - R E N A I S - M	I N D U S T R I E
Natural Cerussite	**Artificial lead white**	**Artificial lead white** : *Wet process + Other Methods*

<u>Natural Cerussite</u> **cannot be dated** by radiocarbon

- **<u>Artificial lead white</u> can be dated** by radiocarbon **<u>if</u>** incorporation of atmospheric CO_2
- Manufacture of lead white from the 4th century until the beginning of the 20th century

⇨ **ABSOLUTE DATING BY RADIOCARBON**

<u>Artificial lead white</u> **cannot be dated** by radiocarbon **RELATIVE DATING**

LSCE

Thèse Cyrielle Messager (2020)

Lucile Beck-2023

Un nouveau matériau pour le ^{14}C !

Ministère de la Culture

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE

ACTUALITÉS
Presse, infographies, évènements

NOUS CONNAÎTRE
Missions, organisation, emploi, formation

AIDES & DÉMARC
Subventions, autorisations, app

En ce moment | Plan VIGIPIRATE | Patrimoine immobilier en péril - mission "Stéphane Bern" | Consultation

Accueil Ministère | Presse | Communiqués de presse

| Françoise Nyssen salue la découverte du Laboratoire de mesure du Carbone 14 qui constitue une avancée

Communiqué de presse

Françoise Nyssen salue la découverte du Laboratoire de mesure du Carbone 14 qui constitue une avancée considérable pour le patrimoine culturel, archéologique et artistique

PUBLIÉ LE 28.06.2018 À 14H00 - PARIS

Françoise Nyssen, ministre de la Culture salue la découverte réalisée par le Laboratoire de mesure du Carbone 14 (LMC14), cofinancé par le ministère de la Cultur

Essonne : au CEA de Saclay, les scientifiques se mettent au ...
Le Parisien - 12 juil. 2019
Dernier zoom sur ARC-Nucléart. Cet atelier laboratoire est principalement basé au **CEA** de Grenoble (Isère), mais les chimistes, physiciens, ...

Le CEA et le CNRS mettent l'atome au service du patrimoine
L'Usine Nouvelle - 17 août 2019
Lucile **Beck** est maître du temps. Docteur de physico-chimie au **CEA** et directrice du laboratoire de mesure du carbone 14 (LMC), elle est ...

Des chercheurs découvrent comment appliquer la méthode ...
Sciences et Avenir - 12 juil. 2019
... de plomb fut abondamment utilisé, notamment dans les peintures à l'huile, pour la réalisation des carnations", nous explique Lucile **Beck**, ...

Restauration des oeuvres d'art : l'atome au service du ...
L'Express - 16 août 2019
Restauration des oeuvres d'art : l'atome au service du **patrimoine** ... dans les locaux du **CEA**, est spécialisé dans la conservation et la ...

Des cosmétiques de l'antiquité datés avec précision

La datation au carbone 14 a été utilisée pour des poudres blanches, synthétisées dans l'ancienne Égypte et la Grèce antique.

MARC CHERKI @mcherki

CHIMIE De manière irréfutable, des chercheurs ont daté des cosmétiques utilisés dans l'ancienne Égypte et la Grèce antique, fabriqués il y a entre 2200 et 3800 ans. Ces dates correspondent à peu près à celles données par les archéologues pour quatre poudres égyptiennes et une grecque, conservées au Musée du Louvre. Les historiens de l'art avaient estimé leurs âges au moyen d'indices : forme des boîtes, matériaux utilisés (bois, roseau, albâtre), lieu des fouilles... Cette correspon-

plomb. *« À ma connaissance, la datation au radiocarbone n'avait jamais été testée pour de la cérusite et de la phosgénite, ce que les chimistes appellent des carbonates de plomb. Or ces pigments blancs ont été très utilisés pendant toute l'histoire de l'art »*, explique Lucile Beck responsable du laboratoire de mesure du carbone 14 à Saclay (CNRS, CEA, IRSN, IRD et ministère de la Culture) et premier auteur de l'article publié dans *Communications Chemistry*.

Blanc de plomb

Pourquoi personne n'avait pensé à cette

ALBERT NICE GODART

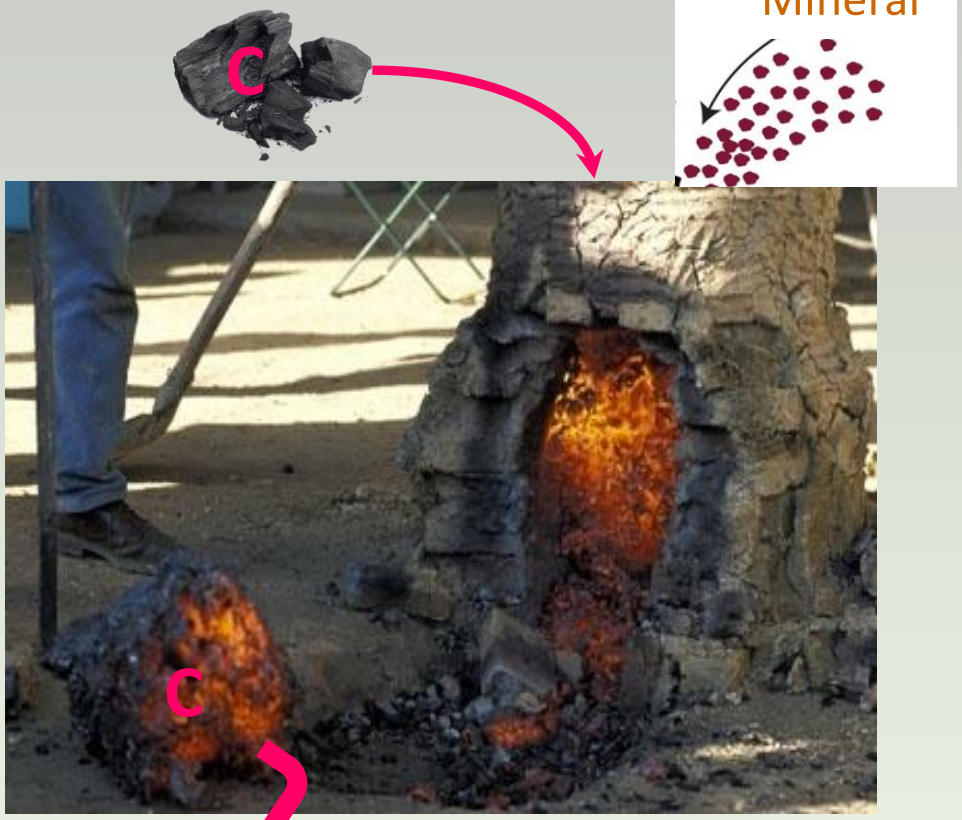
base de plomb, qui ont été synthétisés.

Mais la méthode est destructive. C'est-à-dire qu'il faut retirer un peu de matière de l'objet à dater. L'œuvre d'art est donc altérée par la mesure, même si l'échantillon prélevé n'a que la taille d'une tête d'épingle. Améliorée dans les années 1990, la méthode actuelle utilise un spectroscope de masse avec un accélérateur linéaire de particules. *« Il faut environ 1 mg de carbone, soit 10 à 20 mg de matière à prélever. C'est 100 à 1000 fois moins que pour une datation classique au radiocarbone »*, précise Lucile Beck. Mais à Saclay, les chercheurs veulent encore faire mieux.

Vers d'autres matériaux à faible teneur en C

Charbon de bois

Minerai



Objet

Datation du fer produit par le procédé direct

^{14}C dating

Date de fabrication du métal

Collaboration avec le LAPA (CEA-CNRS) car nécessite au préalable une caractérisation très fine du métal qui contient entre << 1%

Construction des cathédrales

(coll. M. L'Héritier, S. Leroy)

la Croix

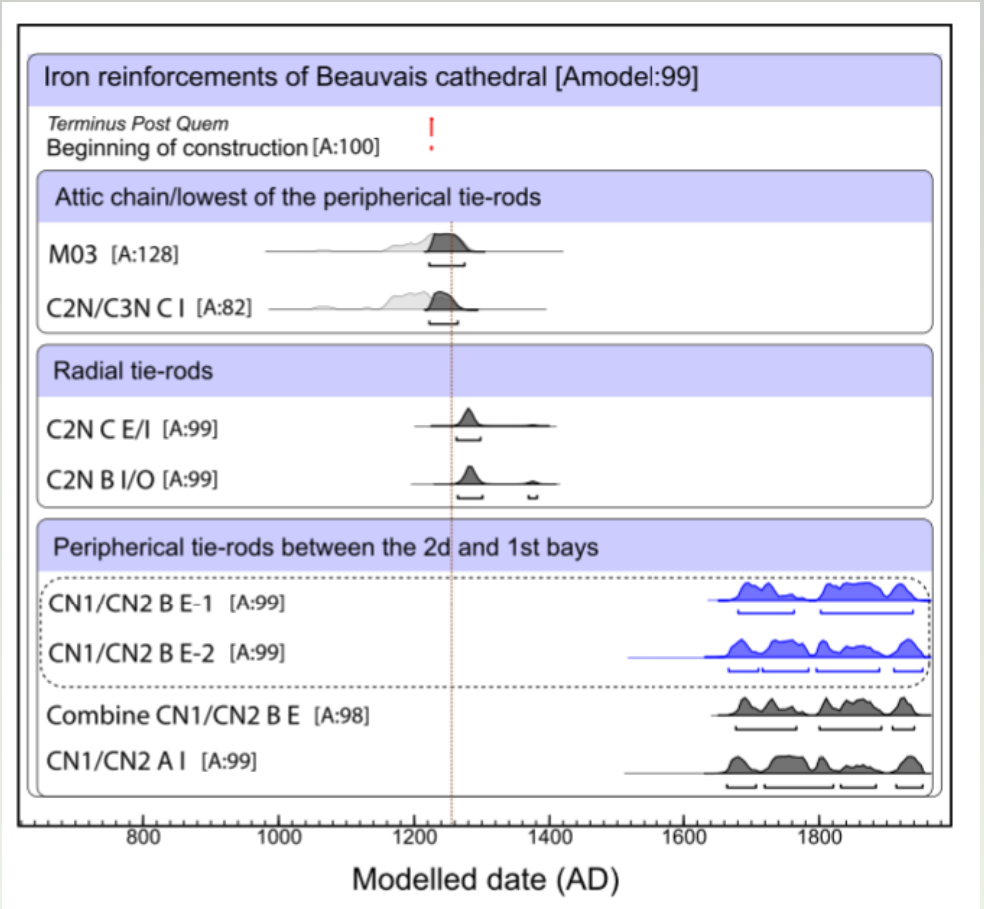
Le secret de la solidité des cathédrales gothiques

En datant par carbone 14 les pièces métalliques retrouvées dans les cathédrales gothiques, des chercheurs français viennent de montrer que le fer était introduit en renfort de la pierre dès l'étape de construction.

P. DILLMANN / CNRS

Des chercheurs ont découvert que le fer était utilisé dans la construction des cathédrales gothiques en renfort de la pierre.

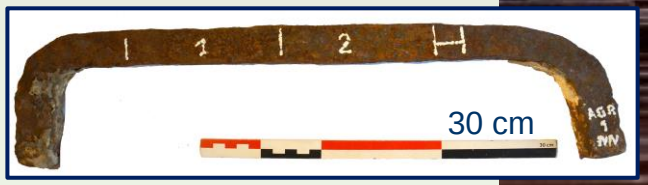
Datation des tirants



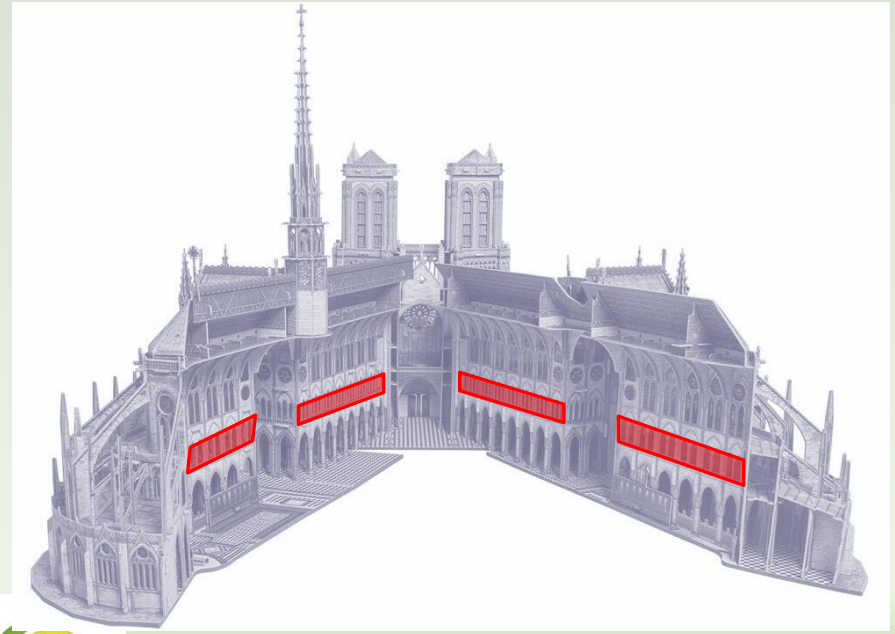
Leroy et al., JAS, 53, 2015

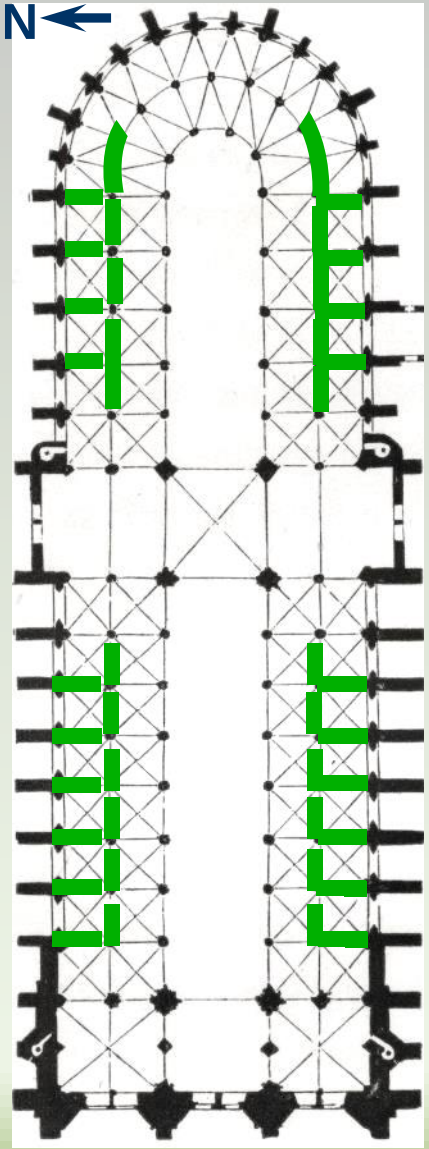
Construction des cathédrales
GT métal de Notre-Dame

(coll. M. L'Héritier, S. Leroy, E. Delqué-Kolic, JP. Dumoulin)


30 cm

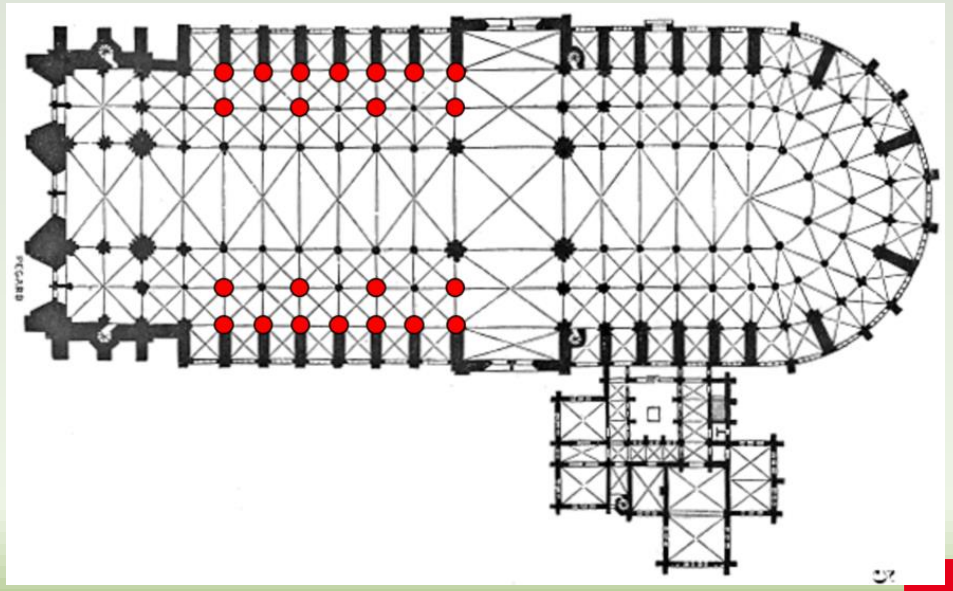
Localisation des fers : agrafes des tribunes





- 7 prélèvements au total (5 dans le chœur, 2 dans la nef)

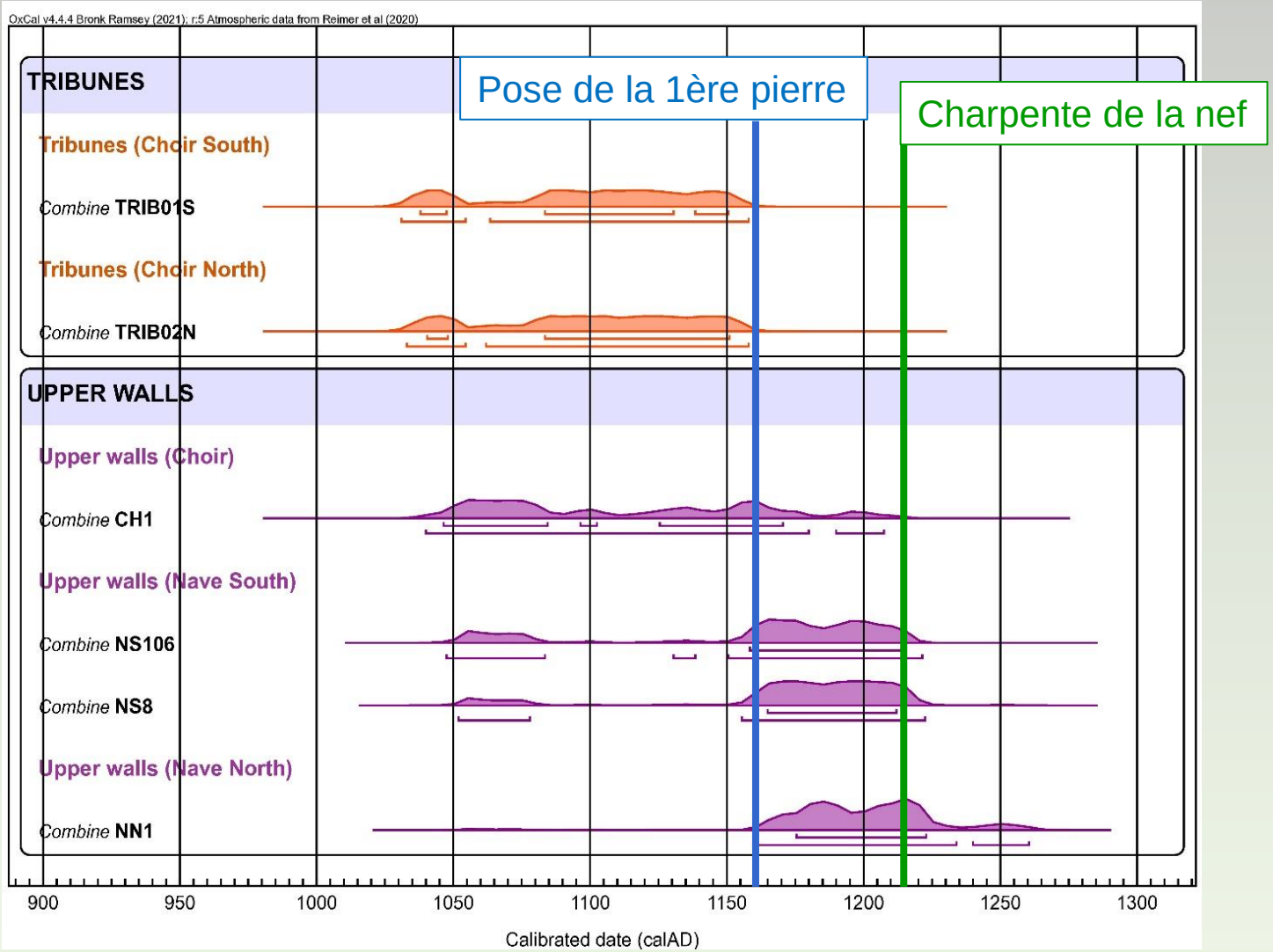
Agrafes des colonnes du collatéral extérieur de la nef



- 1 prélèvement

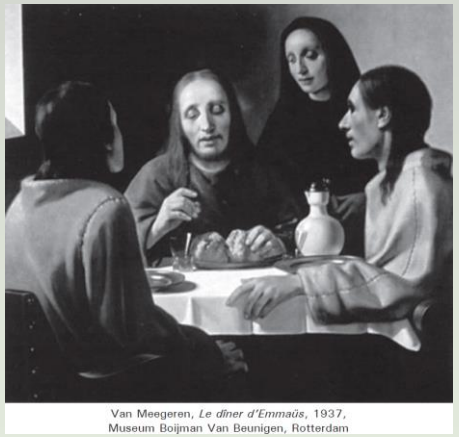
Agrafes des murs-bahuts

a
200 µm


OxCal v4.4.4 Bronk Ramsey (2021); r:5 Atmospheric data from Reimer et al (2020)
TRIBUNES
Tribunes (Choir South)
Combine TRIB01S
Tribunes (Choir North)
Combine TRIB02N
UPPER WALLS
Upper walls (Choir)
Combine CH1
Upper walls (Nave South)
Combine NS106
Combine NS8
Upper walls (Nave North)
Combine NN1
900
950
1000
1050
1100
1150
1200
1250
1300
Calibrated date (calAD)
Pose de la 1ère pierre
Charpente de la nef

Art forgeries

"Millions of counterfeit art works are circulating in the online environment"



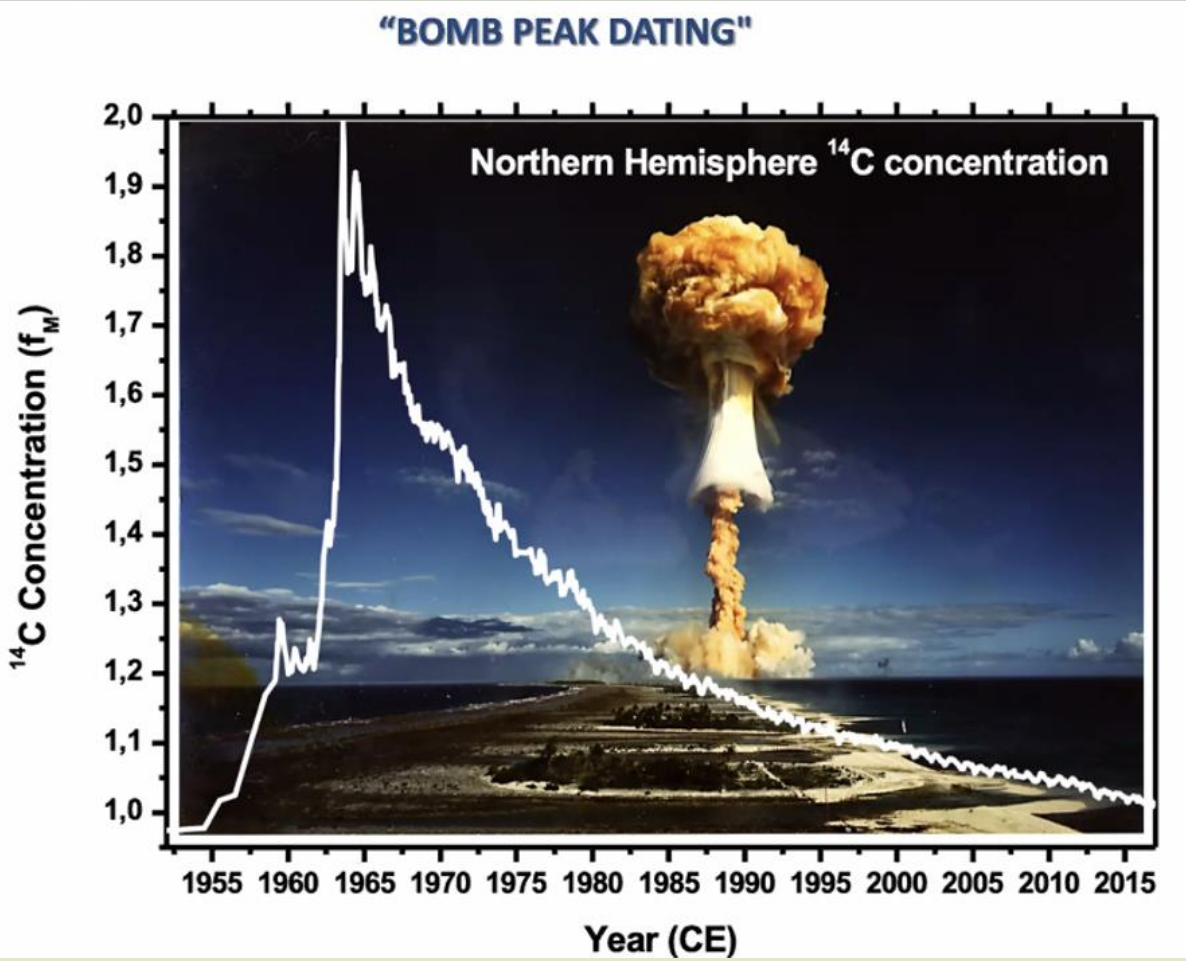
Van Meegeren, *Le dîner d'Emmaüs*, 1937,
Museum Boijman Van Beunigen, Rotterdam

*Vermeer, Hals/**Van Meergeren***

The exhibition of 30 paintings in Genoa, Italy was shut down three days early on July 13th, 2017
After careful examination, experts confirmed that 20 of the 21 paintings seized by the prosecutors were forgeries.

Alberto Giacometti's *Walking Man*.

Detecting painting using ^{14}C



^{14}C a longtemps été considéré comme :

- Trop invasive

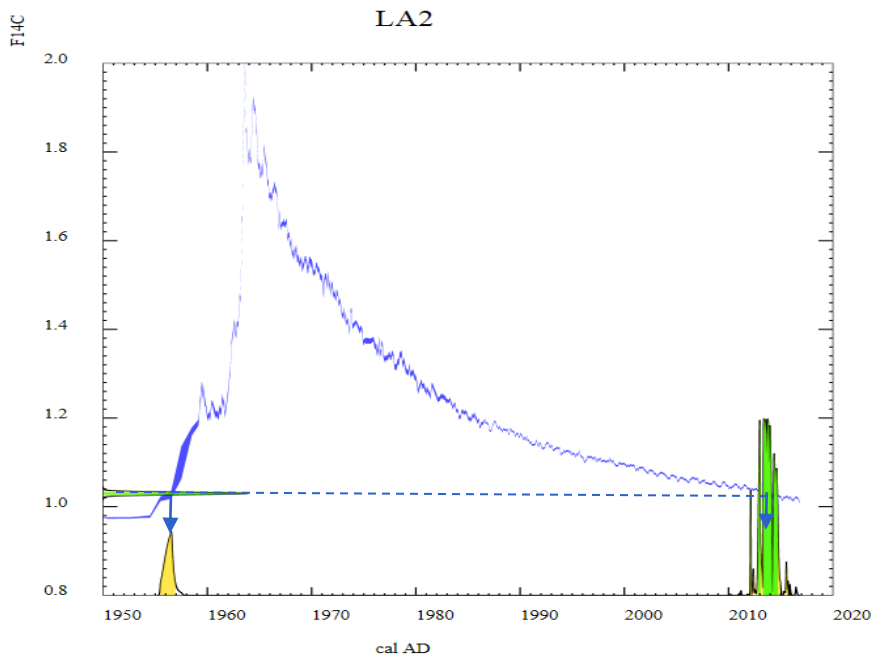
→ SMA

- Trop imprécise
- → Essais nucléaires et le "pic des bombes"

Atmospheric nuclear tests carried out in atmosphere after 1950 resulted in an increase of the ^{14}C concentration by almost a factor 2 in the mid 1960s

Bomb peak: “the nuclear option”

- **^{14}C value ($F^{14}C$) :**
- **1.0301 ± 0.0027**



Two solutions:

1955 – 1956 **2012 – 2014**

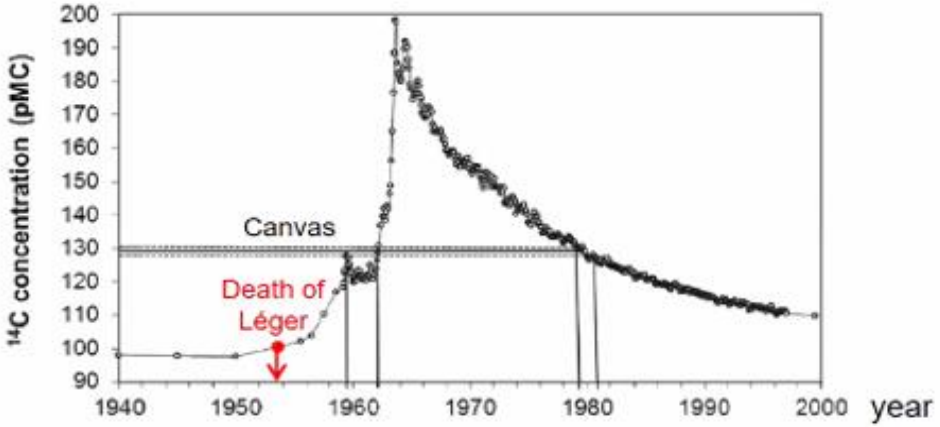
☺ Résolution élevée
☺ Courbe bien documentée
☺ Logiciel de calibration disponible gratuitement et facile à utilizer

☹ 2 solutions

Contraste de formes, Fernand Léger (?)
Peggy Guggenheim Collection, Venice

Contraste de formes, Fernand Léger (1881-1955), 1913,
Solomon G. Guggenheim Foundation, New York

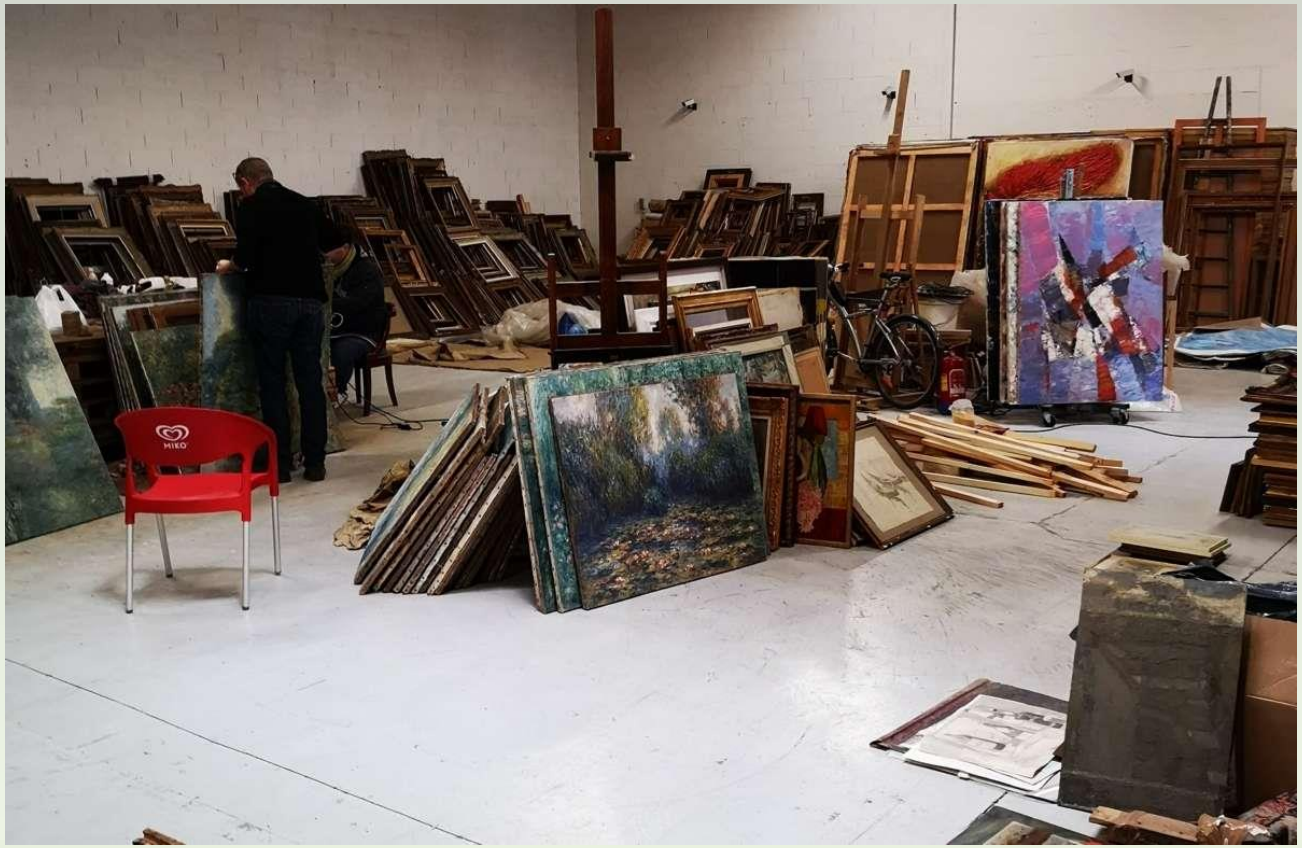
Detail of the canvas sample



L. Caforio et al., Discovering forgeries of modern art by the ^{14}C bomb peak, *Eur. Phys. J. Plus* **129**:6 (2014)

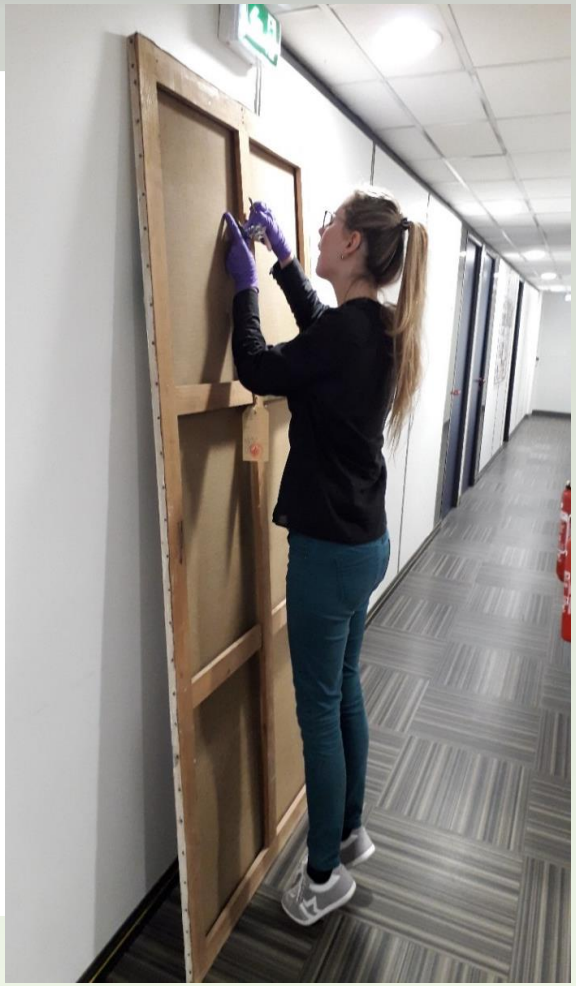
Radiocarbon dating of seized paintings

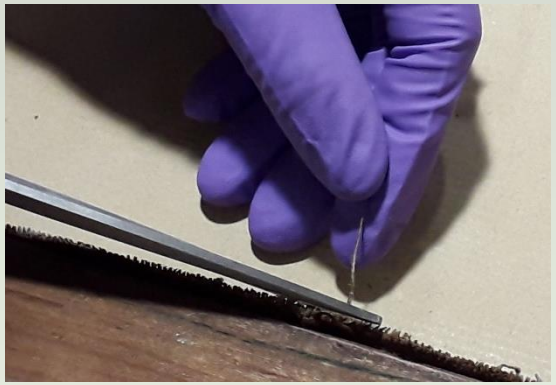
- Hundreds of paintings were discovered in a restorer's workshop by the French *Central Office for the Fight against Illicit Trafficking in Cultural Property (OCBC)*
- From Impressionist period to contemporary art



Challenges working in the context of a police investigation

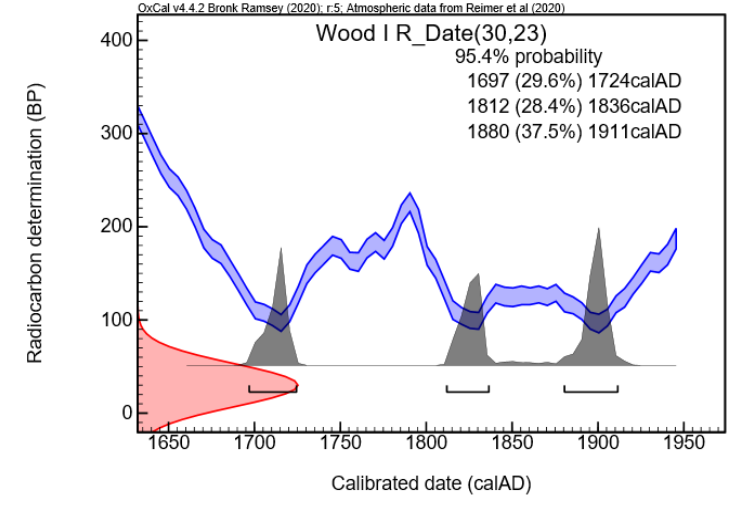
- ❑ No documentation
- ❑ No previous studies
- ❑ Confidentiality
- ❑ Time and sampling limitations:
  - only one campaign for sampling and short deadline for reporting
- ❑ No guarantee of results





Dater le chassis en bois

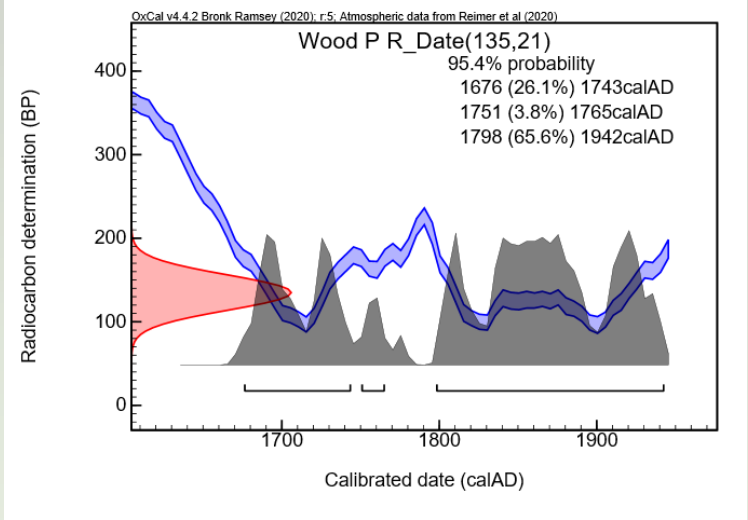
Impressionist

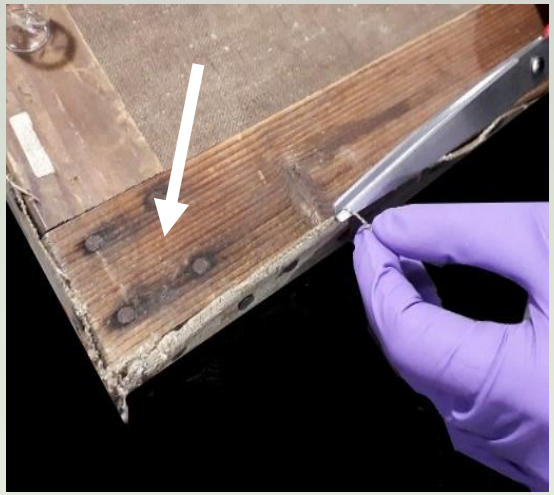


1697 – 1724
1812-1836
1880- 1911

→ < 1947

Post-impressionist



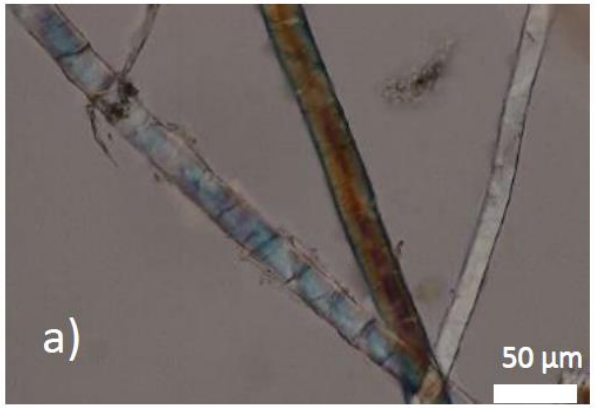


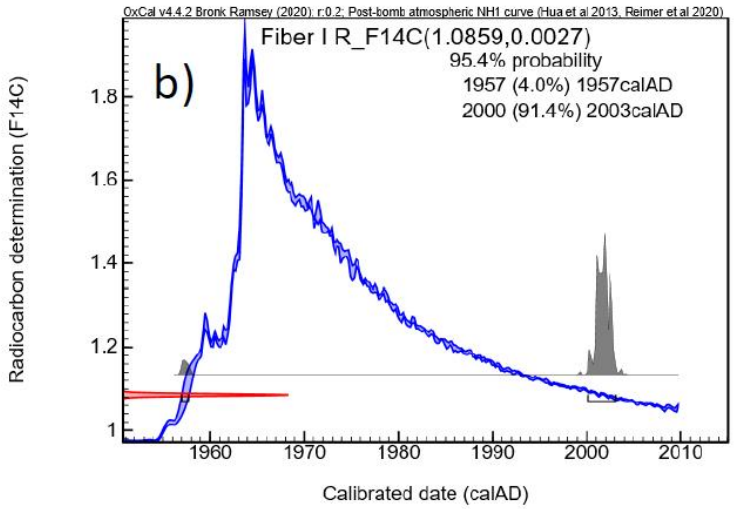
1676 – 1743
1751-1765
1798- 1942

→ < 1943

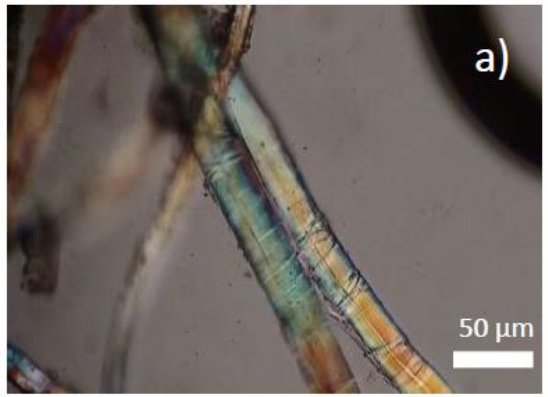
Dater la toile

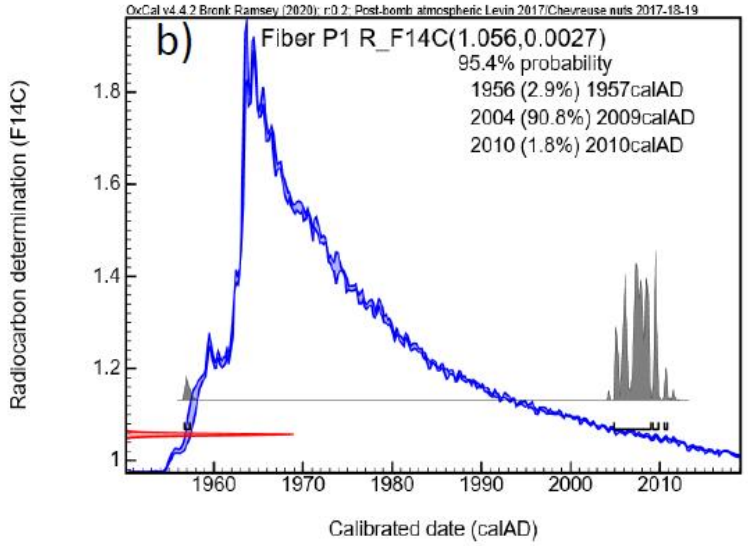
Impressioniste





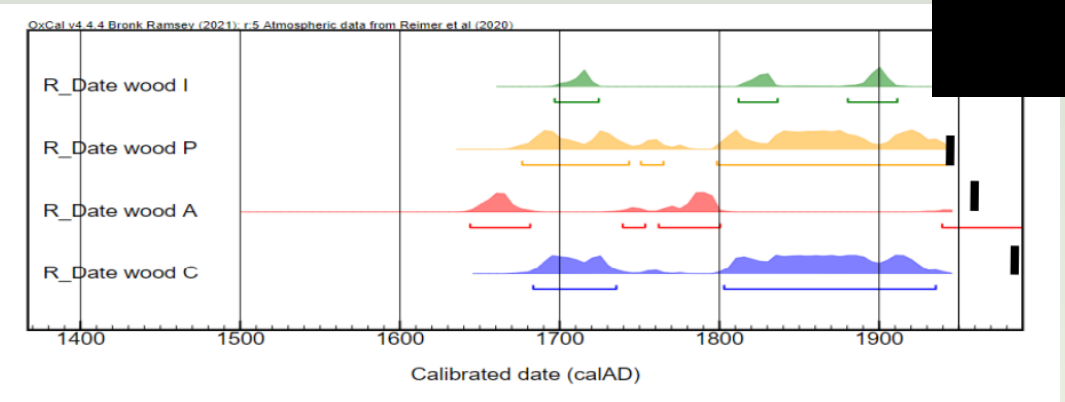
Post-impressioniste

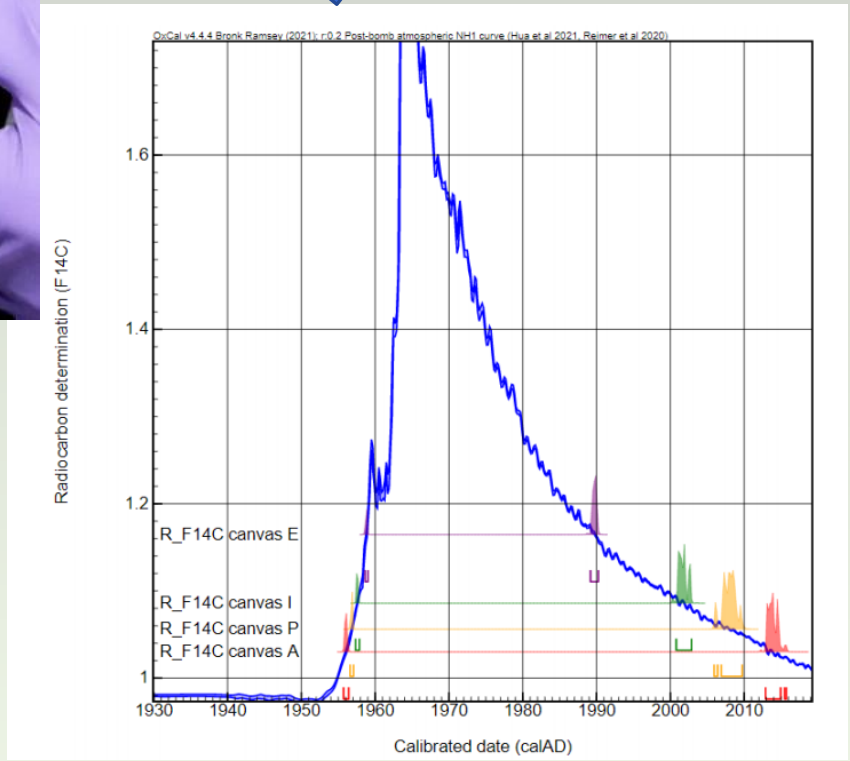




- 1) Identification des fibres
- “Bast fibers” → lin
- 2) Les plantes qui ont servi à faire les fibres de textiles ont été récoltées :
- - en 1957 ou entre 2000 et 2003 pour la peinture impressioniste (l’artiste suppose est mort en 1947)
- - en 1956-1957 ou entre 2004 et 2010 pour la peinture post-impressioniste (l’artiste suppose est mort en 1943)

Dater la toile est la solution !





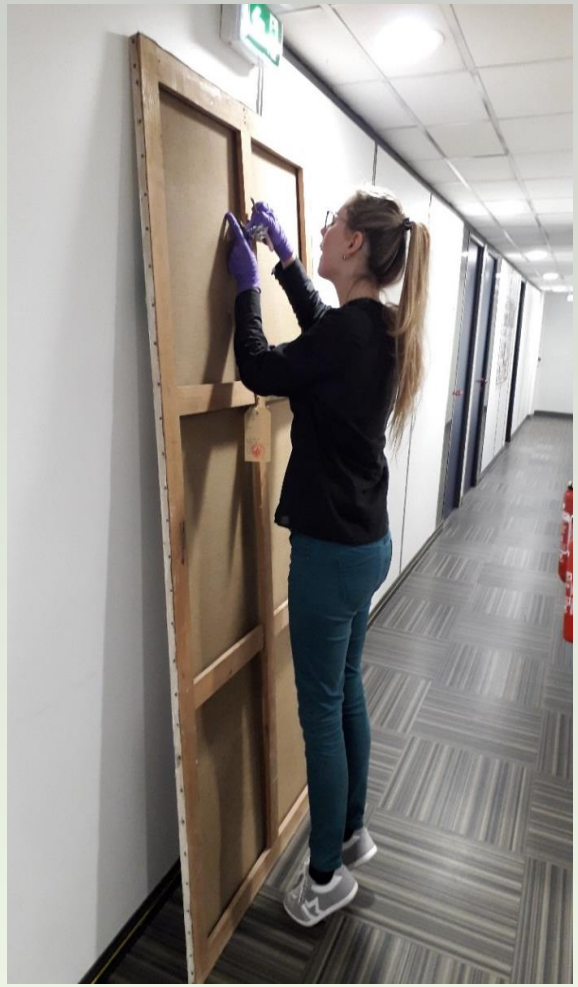
Dates avant 1950 → Anciens bois ou châssis sélectionnés par les faussaires

Toiles après 1955 → peinture après1955

Beck, Physics 4, (2022) 462–472

Défis du travail dans un context d'enquête policière

- ✓ Pas de documentation, pas de dossiers d'oeuvre, pas d'étude préalable
- ✓ Confidentialité
- ✓ Pas de garantie de résultats
- ✓ Temps compté et échantillonnage limité
- ✓ Une seule campagne et délai très court pour rendre les résultats
  - ✓ First contact: 6th of February
  - ✓ Sending quotation to the judge: 22d of February
  - ✓ Approval of the judge received the 27th of April asking the results to be obtained before the 15th of June!
  - ✓ Samples taken the 16th of May at OCBC premises
  - ✓ Sample preparation, 14C measurements, data analysis, reporting
  - ✓ Report delivered the 18th of June!



But successful story finally and non-ambiguous results!

ATOMS FOR HERITAGE
IAEA

Forensic Science International 333 (2022) 111214

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Detecting recent forgeries of Impressionist and Pointillist paintings with high-precision radiocarbon dating

Lucile Beck[a,*], Ingrid Caffy[a], Solène Mussard[a], Emmanuelle Delqué-Količ[a], Christophe Moreau[a], Marc Sieudat[a], Jean-Pascal Dumoulin[a], Marion Perron[a], Bruno Thellier[a], Stéphane Hain[a], Eddy Foy[b], Christophe Moulherat[c], OCBC[d]

Special issue IAEA CRP Nuclear Technologies for Foren

physics

Article

Ion Beam Analysis and ^{14}C Accelerator Mass Spectrosc Identify Ancient and Recent Art Forgeries §

Lucile Beck

Physics **2022**, 4, 462–472. https://doi.org/10.3390/physics4020031

Le Monde

SCIENCES • ARTS

Quand les essais nucléaires trahissent les faussaires

Le Laboratoire de mesure du carbone 14 a pu montrer, grâce au « pic des bombes » dans les années 1960, que des toiles saisies par l'Office central de lutte contre le trafic de biens culturels avaient été peintes après la mort de leurs auteurs présumés.

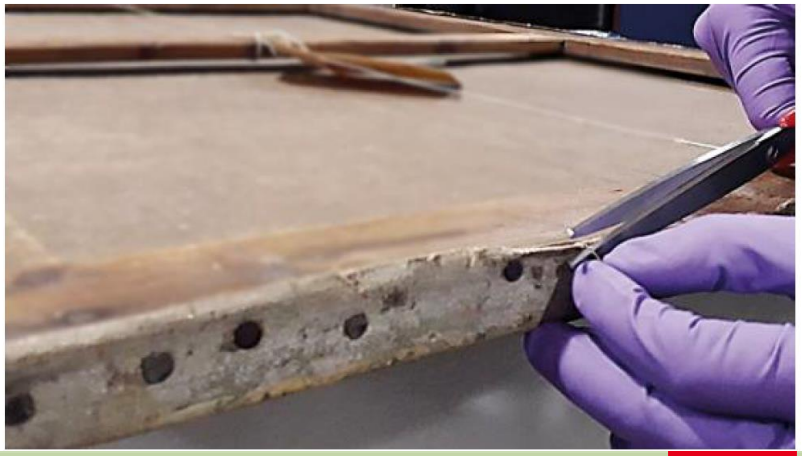
Par Pierre Barthélémy

IAEA
International Atomic Energy Agency

Truth-Revealing Atoms

Accelerator-based analytical techniques detect art forgeries

Joanne Liou



Forged artwork could pollute humanity's understanding of history, researchers say.

RADIOCARBON DATING HELPS POLICE IDENTIFY FORGED PAINTINGS

Advances in the technique have bolstered its reputation as a tool for investigating faked artwork.

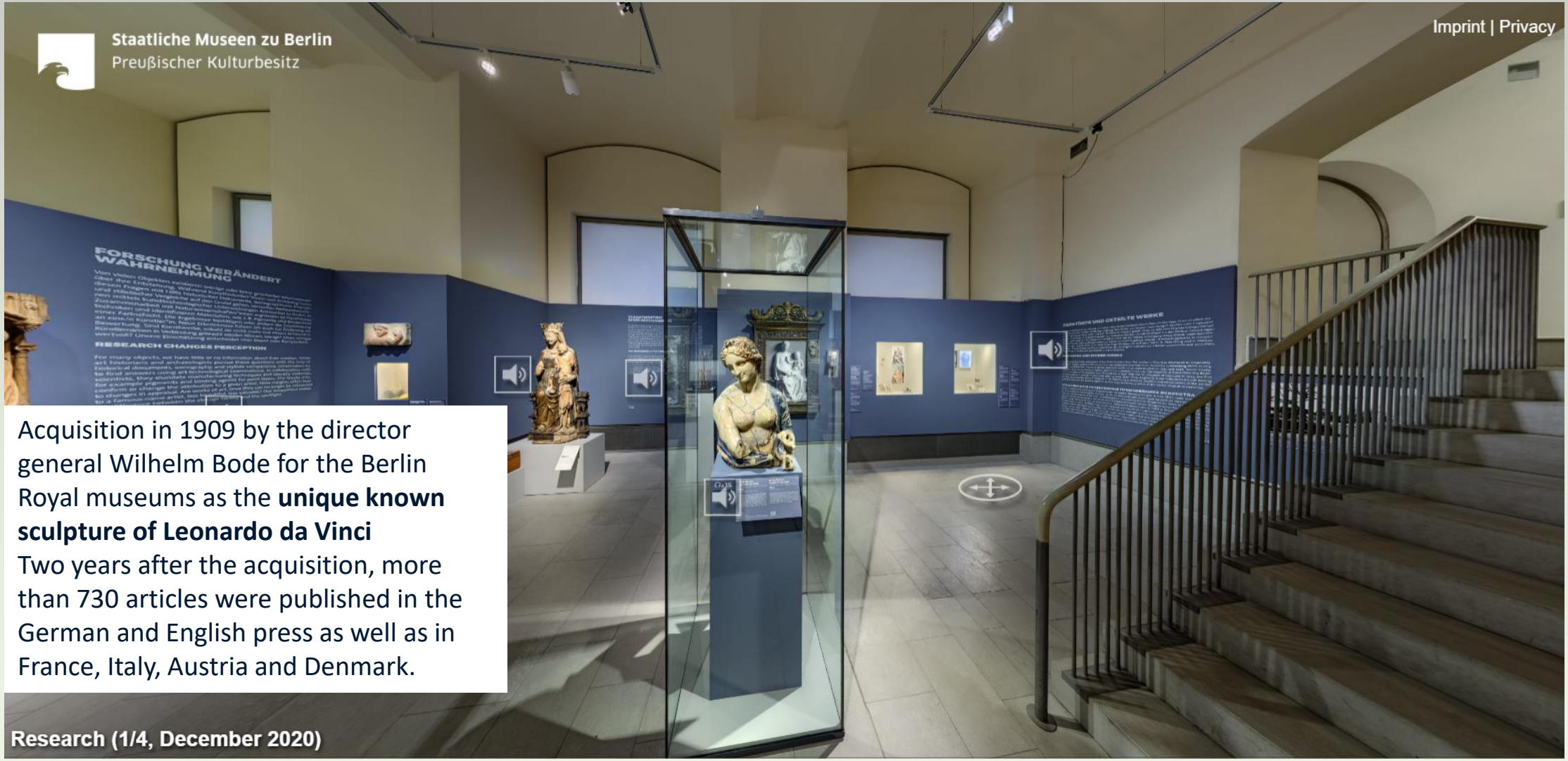
By Carolyn Wilke

Radiocarbon dating has unmasked two forged paintings in France — probably the first time the technique has been used in a police investigation. The paintings were supposedly impressionist and pointillist works from around the early twentieth century. But a team led by heritage scientist Lucile Beck at the University of Paris-Saclay used radiocarbon levels in the fibres of their canvases to date them to sometime within the past 70 years. The researchers concluded that the paintings are modern forgeries in a 4 February report — and therefore valuable — they don't want the collection of larger samples to damage it, says art historian Anna Tummers at Leiden University in the Netherlands, who was not part of the new research.

The technique's success might persuade more of the art world to seek radiocarbon dates, which can more definitively pinpoint when a painting was made, Tummers says. Researchers typically use imaging and chemical analysis to sniff out art forgeries. These methods can peer beneath brushstrokes to see how a painting's materials have aged, but they cannot conclusively nail down a painting's date.

Nature 603 | 17 March 2022

Attribution d’un oeuvre d’art : la Flora



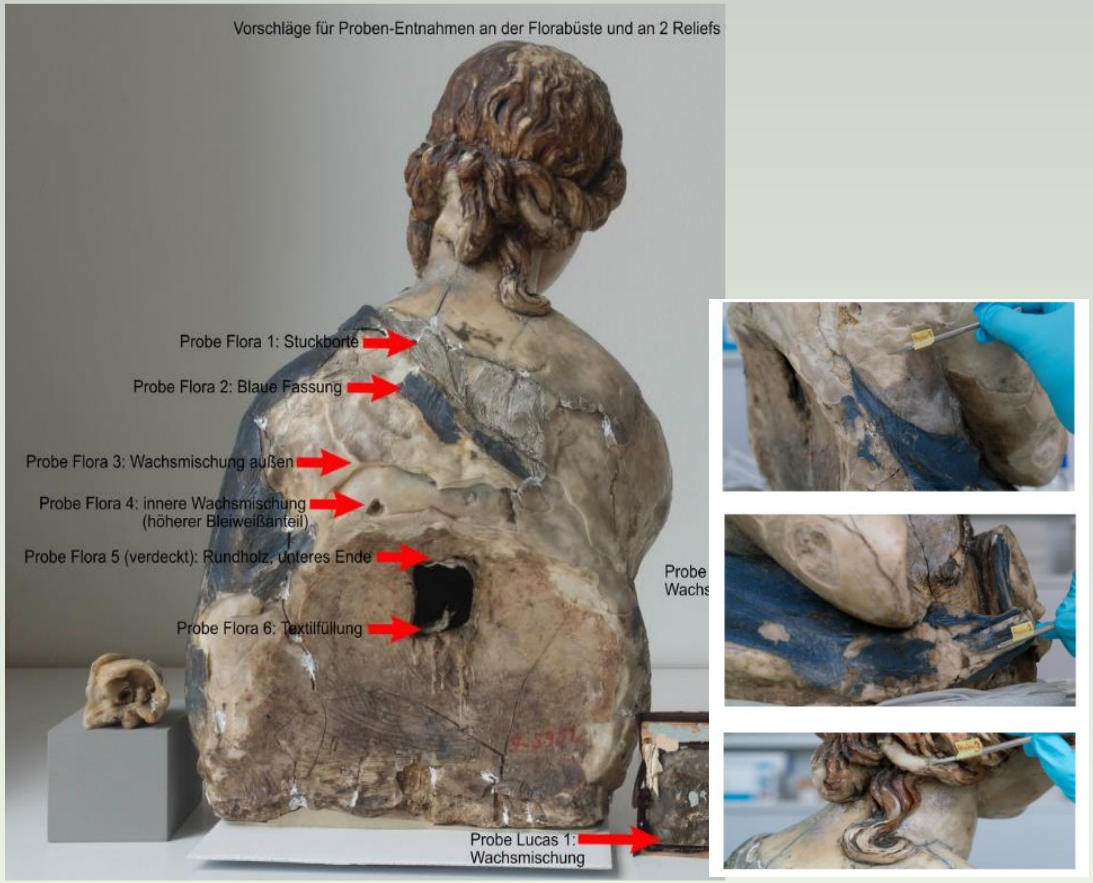
Acquisition in 1909 by the director general Wilhelm Bode for the Berlin Royal museums as the **unique known sculpture of Leonardo da Vinci**

Two years after the acquisition, more than 730 articles were published in the German and English press as well as in France, Italy, Austria and Denmark.

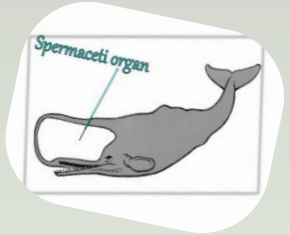
Doute sur son authenticité

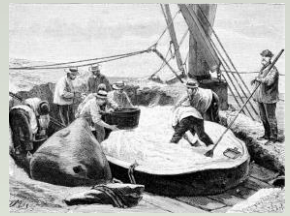
Attribution d'un oeuvre d'art : la Flora

Study conducted by I. Reiche (Rathgen Forschungslabor & C2RMF, PSL)



- 7 wax samples (unusual material coming from sperm whale, called spermaceti/blanc de baleine)





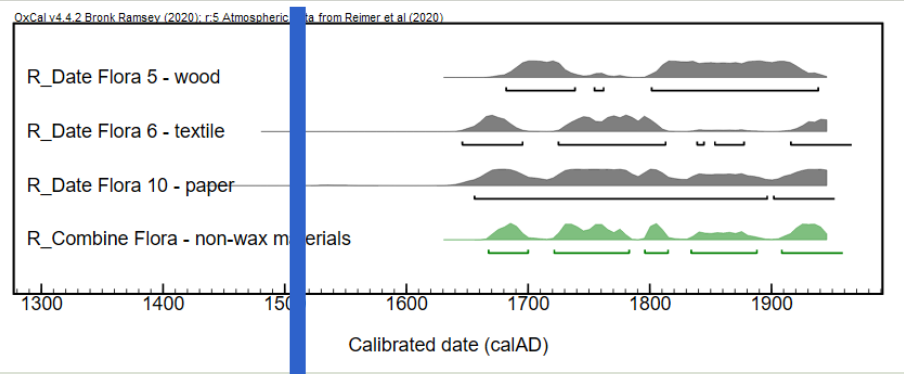
used for candles, cosmetics, pharmacy from 1750

- 3 other samples: wood, paper and textile

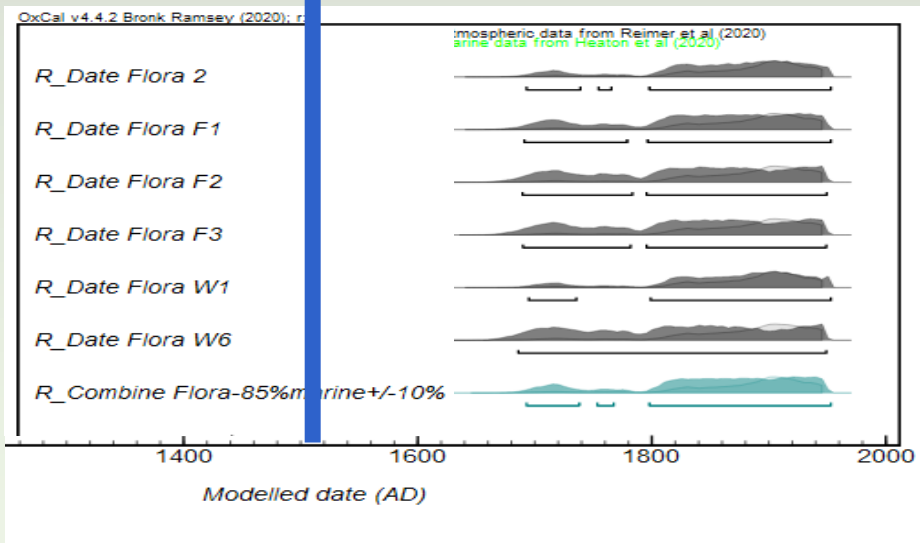
9 dates sur 4 matériaux différents

Death of Leonardo da Vinci

Terrestrial samples
Wood, paper, textile
After 1670



Wax samples (Spermaceti + beeswax)
After 1707



scientific reports

OPEN

New results with regard to the Flora bust controversy: radiocarbon dating suggests nineteenth century origin

Ina Reiche, Lucile Beck & Ingrid Caffy

Radiocarbon, Vol 00, Nr 00, 2022, p 1–10 DOI:10.1017/RDC.2022.79
Selected Papers from the 3rd Radiocarbon in the Environment Conference, Gliwice, Poland, 5–9 July 2021.
© The Author(s), 2022. Published by Cambridge University Press for the Arizona Board of Regents on behalf of the University of Arizona

MARINE RESERVOIR EFFECT OF SPERMACETI, A WAX OBTAINED FROM THE HEAD OF THE SPERM WHALE: A FIRST ESTIMATION FROM MUSEUM SPECIMENS

Lucile Beck* • Ingrid Caffy • Emmanuelle Delqué-Količ • Jean-Pascal Dumoulin • Stéphane Hain • Christophe Moreau • Marion Perron • Marc Sieudat • Bruno Thellier • Charlotte Van Hove

https://www.smb.museum/en/whats-new/detail/?tx_smb_pi1%5BnewUid%5D=2125&cHash=ddbaa2b7cda2645cff6c0658592e403f

Museums & institutions Research Exhibitions Education and outreach Events

From Fake Flora to a Gold Robbery: A Virtual Tour through the History of the Bode-Museum

13.04.2021

Bode-Museum

ART HISTORY NEWS
Research. Exhibitions. Auctions. Discoveries. Opinions.

about articles contact & contribute

edited by Bendor Grosvenor and Adam Busiakiewicz

Bode Museum Finally Describes their 'Leonardo' as 'Manner of'

April 20 2021

Posted by Adam Busiakiewicz:

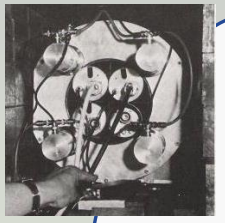
The Bode Museum in Berlin have finally come round to re-cataloguing a dubious sculpture in their collection as 'In the manner of Leonardo Da Vinci'.

The above sculpture of Flora was purchased as a Leonardo in full in 1909 by the then director of Prussian art collections, Wilhelm von Bode. However, recent analysis by the French National Centre for Scientific Research (CNRS) has concluded that the piece must be a nineteenth century imitation. Scientific analysis has shown that the majority of the sculpture is made from spermaceti wax, a type of wax harvested for candles during the nineteenth century. Strong comparisons have been made with several works by the sculptor Richard Cockle Lucas (1800-1883), who has been suggested as the likely creator of the piece.

Update - A reader has kindly alerted me to the fact the sculpture is included within a new exhibition on the museum's history entitled *Klartext* (Plain Talk). A free virtual tour of the exhibition, plus audio guides, can be accessed here.

Merci pour votre attention !

En France



1954

Saclay/Gif
CFR/LSCE
14 000 éch

2010

1983

Gif/Saclay
Tandétron
13 000 éch

2003

1965
Lyon
CDRC
18 000 éch
(+16 000 preparés)

Paris VI
Orsay
ORSTOM
Nancy
Monaco
Marseille
Bordeaux
…

Paris
C2RMF
MNHN
(prépa.)

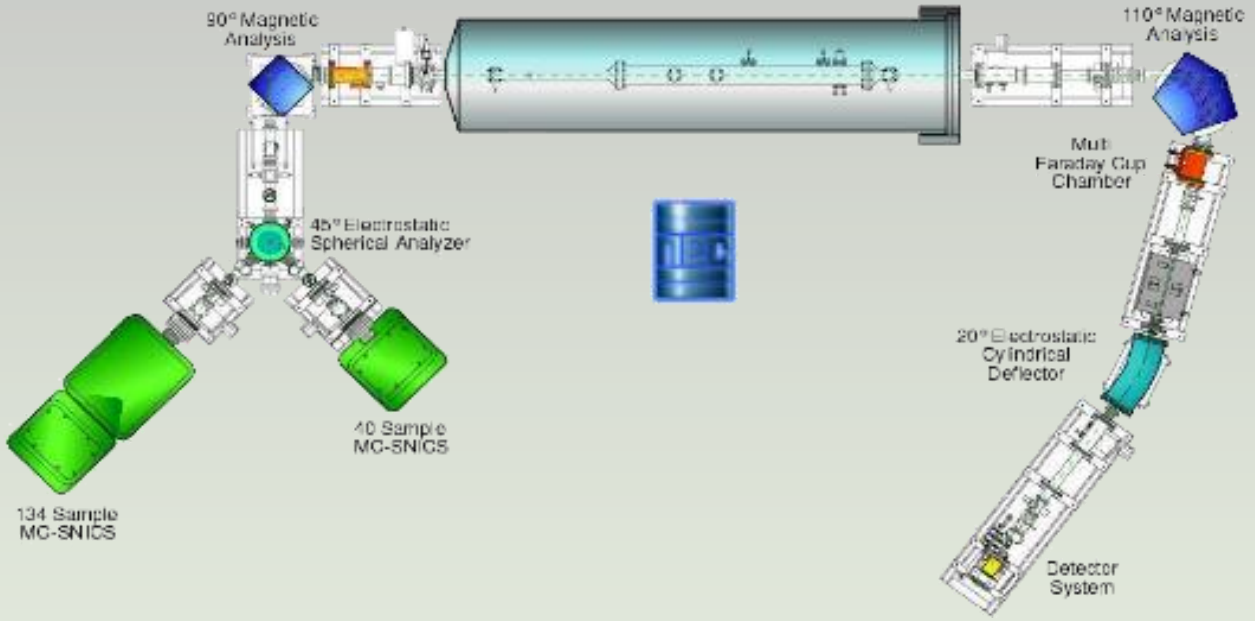
2015
Saclay-Orme
EchoMicadas
7 300 éch

2003
Saclay
*56 000 éch **

2016
Aix en P.
AixMicadas

*dont 12000 préparés à Lyon et Paris

SMA ARTEMIS au LMC14

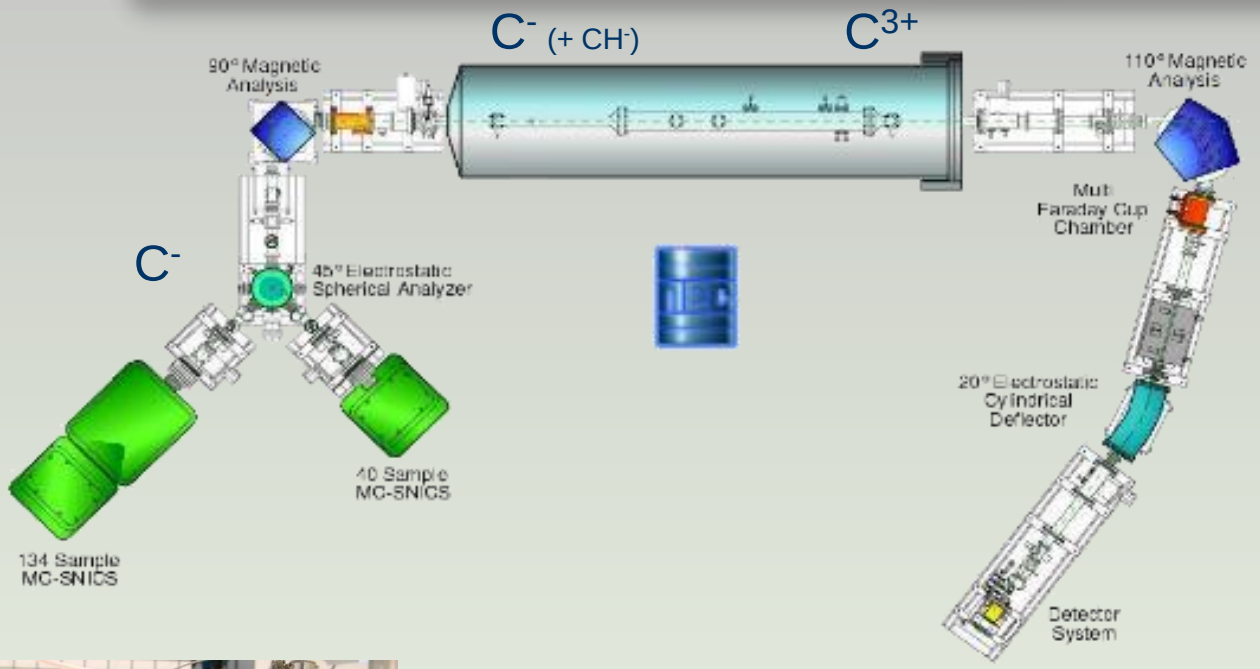


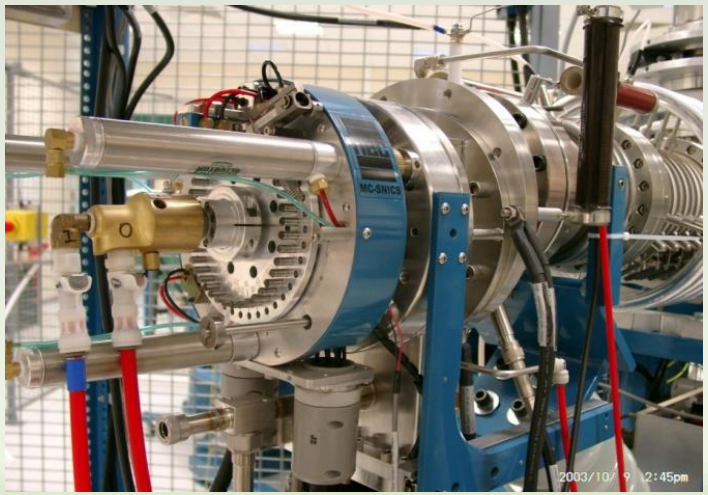
- Commandé en 2001
- 1ère mesure en 2003
- 1 ingénieur, 2 techniciens

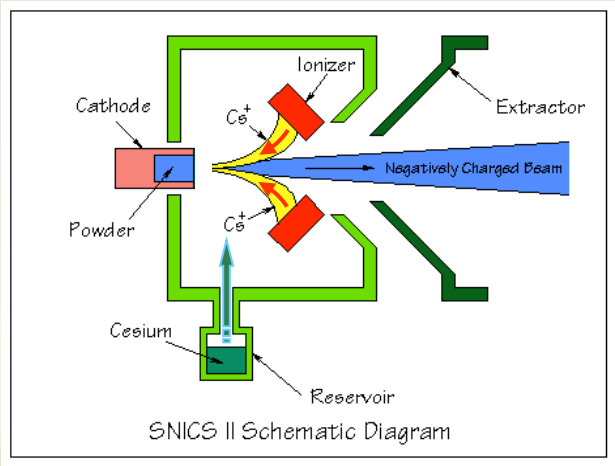
Tandem accelerator

- 3 MV Pelletron tandem (NEC type 9SDH-2)
- Terminal voltage operation : 2.6 MV
- Ar gas stripper (molecules break & charge exchange)
- Final charge states : from 1+ to 4+

SMA

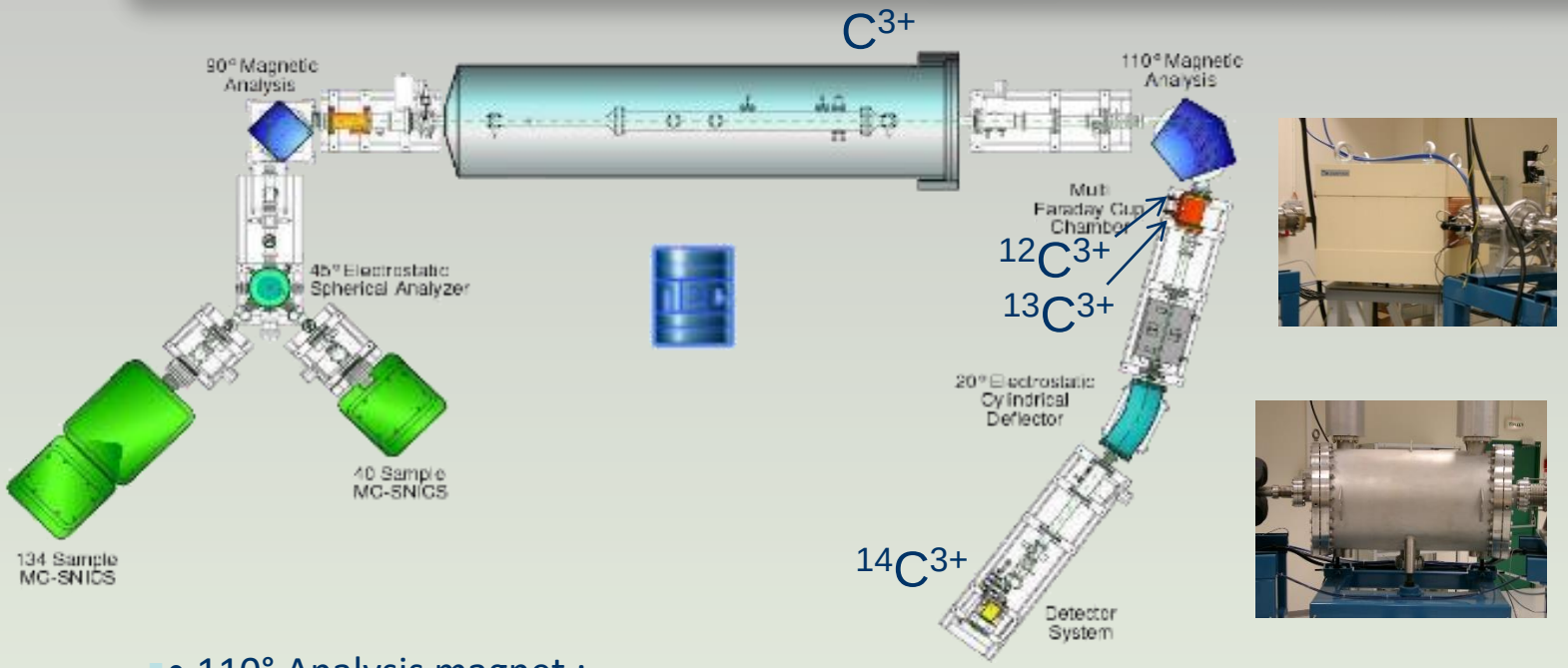






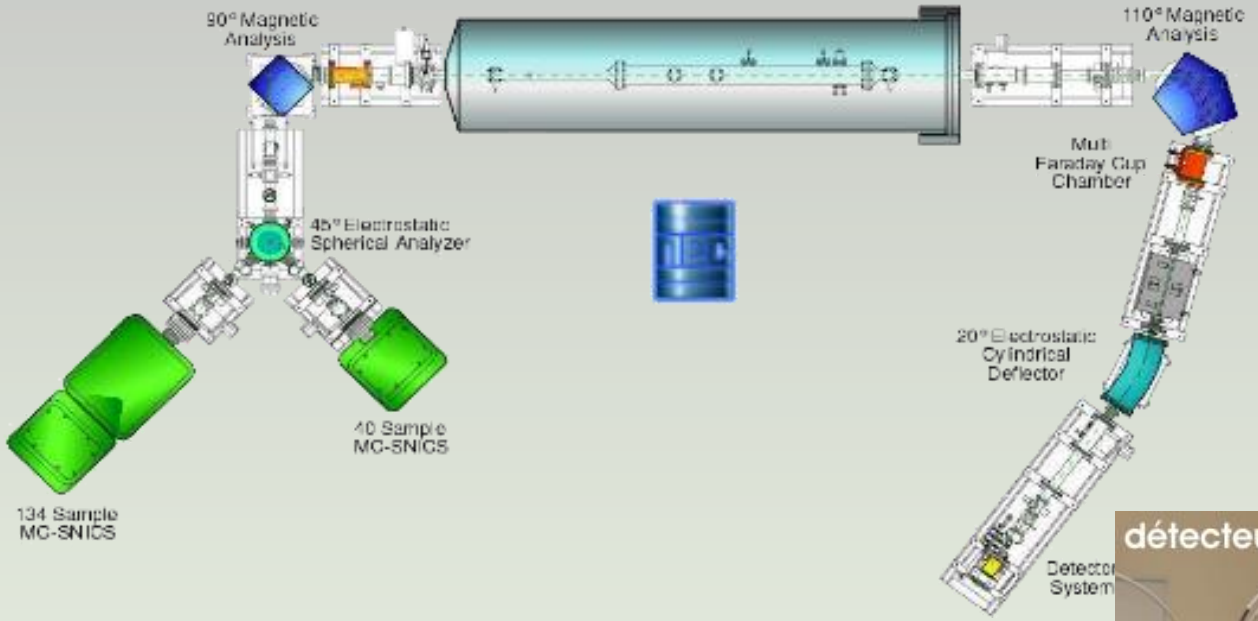
- Two MC-SNICS Cesium sputter ion sources of 40 and 134 samples
- Automated sample changer for high rate measurement
- 18 kV power supply to extract negative ions from the source coupled with a 45 kV power supply to accelerate the negative ions up to 63 keV in order to enter in the accelerator.

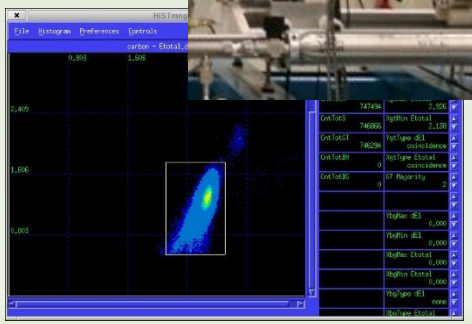
SMA



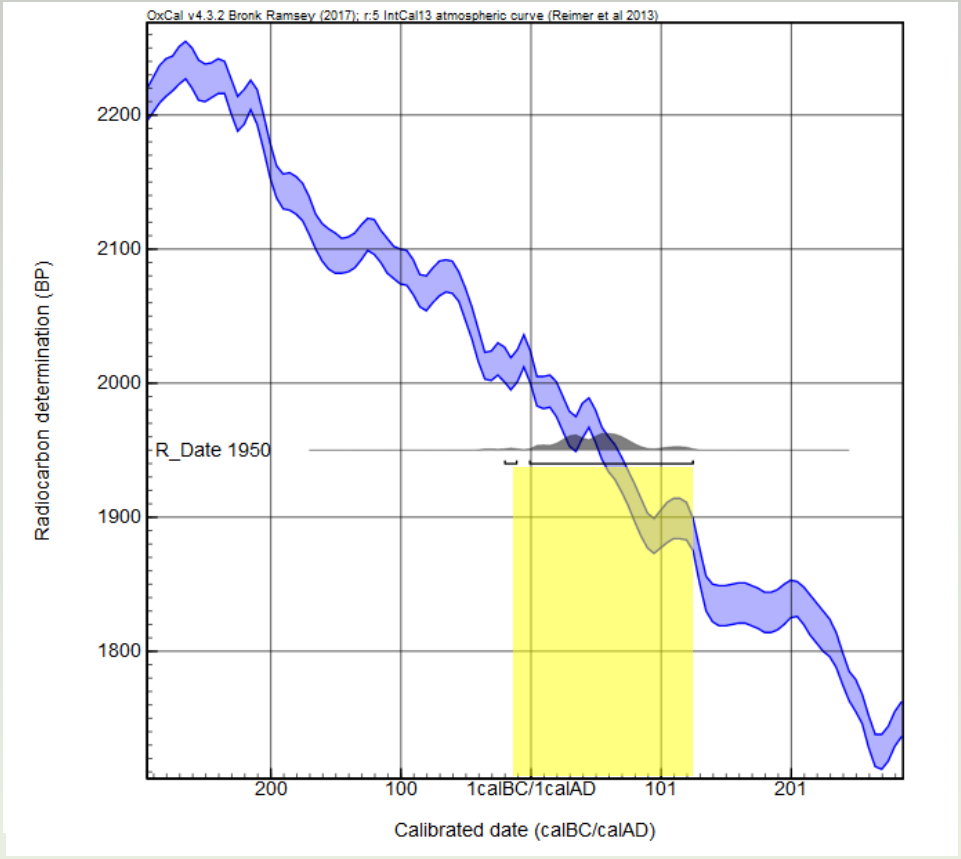
- 110° Analysis magnet :
- Selection in mass, charge (3+) and Energy
- Off line Multi Faraday cup to measure $^{12}C^{3+}$ and $^{13}C^{3+}$
- electrostatic quadrupole analyser ECA (focusing)
- 20° Electrostatic Cylindrical Analyser :
- Selection in Energy and charge

SMA

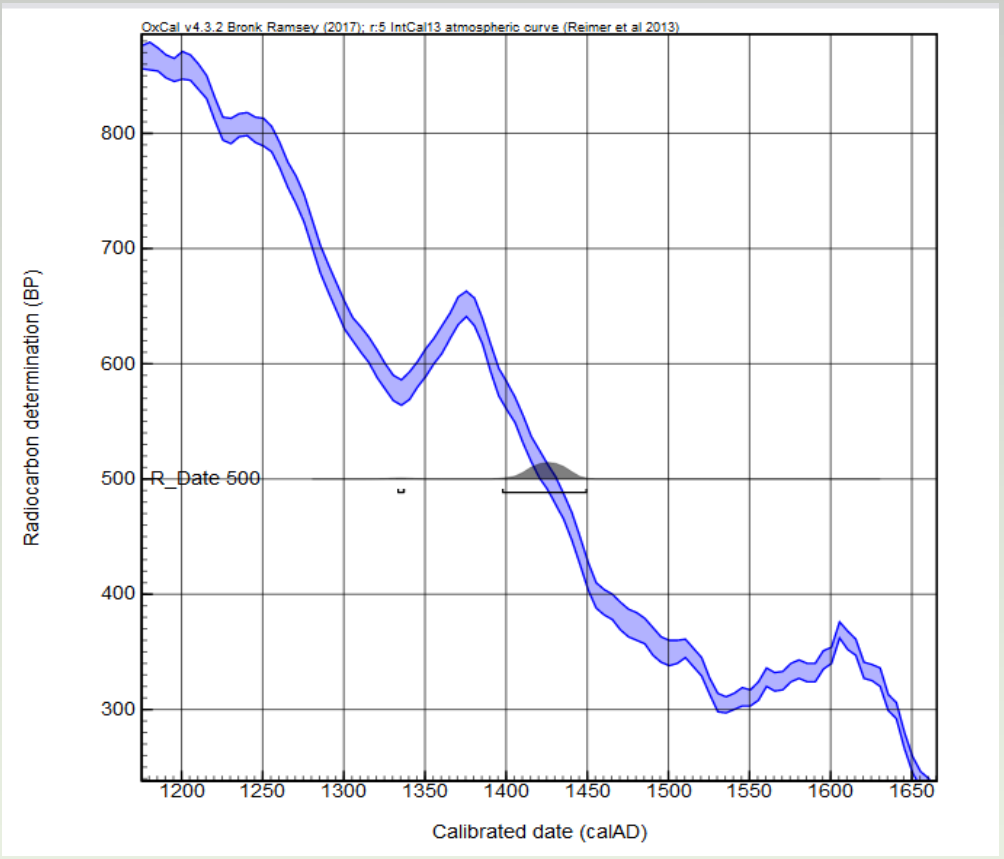




- Ionization chamber filled with Ar (90%) CH_4 (10%) mixture.
- Detection of the $^{14}C^{3+}$ ions



21 av. J.-C. -125 ap. J.-C.



1398 – 1449 ap. J.-C.

1977

ARTICLE

Radioisotope Dating with a Cyclotron: The sensitivity of radioisotope dating is improved by counting atoms rather than decays.

REPORT

Radiocarbon Dating with Electrostatic Accelerators: Dating of Milligram Samples

BY C. L. BENNETT, R. P. BEUKENS, M. R. CLOVER, D. ELMORE, H. E. GOVE, L. KILIUS, A. E. LITHERLAND, K. H. PURSER • SCIENCE • VOL. 201, NO. 4353 • **28 JUL 1978** : 345-347

The recently developed direct counting technique for radiocarbon atoms has been used to measure the relative numbers of such atoms in various geological samples which had earlier been dated by the beta-ray counting method. Sample weights ranged ...

REPORT

Radiocarbon Dating Using Electrostatic Accelerators: Negative Ions Provide the Key

BY C. L. BENNETT, R. P. BEUKENS, M. R. CLOVER, H. E. GOVE, R. B. LIEBERT, A. E. LITHERLAND, K. H. PURSER, W. E. SONDHEIM • SCIENCE • VOL. 198, NO. 4316 • **04 NOV 1977** : 508-510

Mass spectrometric methods have long been suggested as ways of measuring $^{14}C/^{12}C$ ratios for carbon dating. One problem has been to distinguish between ^{14}N and ^{14}C. With negative ions and a tandem electrostatic accelerator, the ^{14}N background is ...