



Li-Hill, 2019, Grenoble

Applications des micro-faisceaux synchrotron à l'ESRF pour l'étude des matériaux du patrimoine

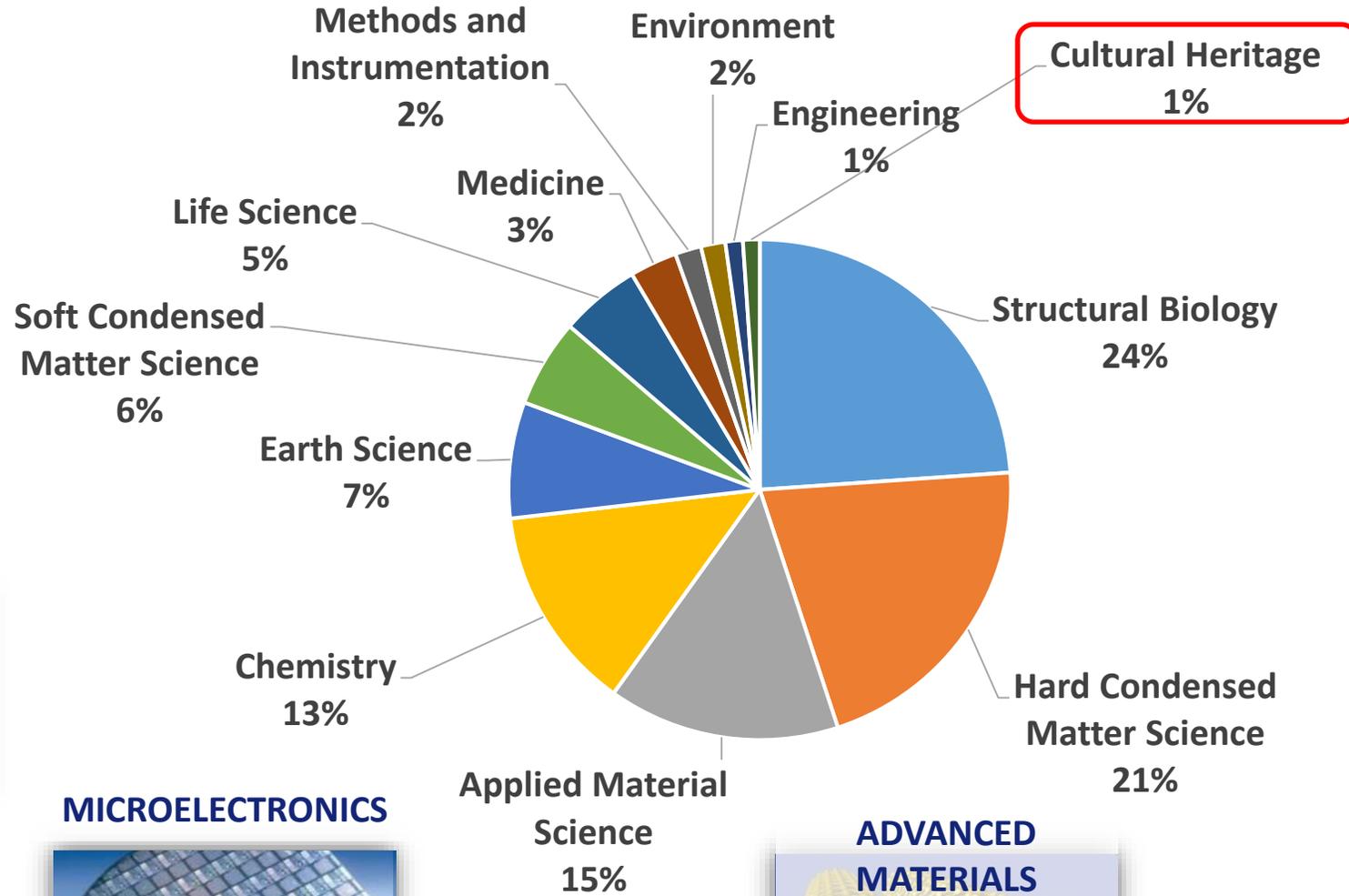
Marine Cotte

¹ *ESRF (Synchrotron Européen),
71 avenue des martyrs, 38000 Grenoble (France)*

² *Laboratoire d'Archéologie Moléculaire et Structurale,
CNRS UMR 8220, Sorbonne Universités, Univ Paris 06, 4 place
Jussieu 75005, Paris (France)*



Allocated beamtime in 2021



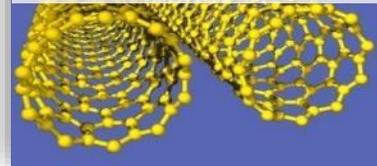
PETROCHEMICALS



MICROELECTRONICS



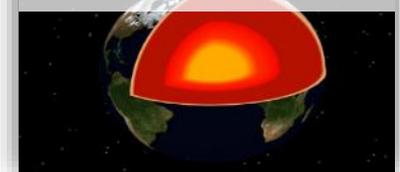
ADVANCED MATERIALS



HEALTH & FOOD

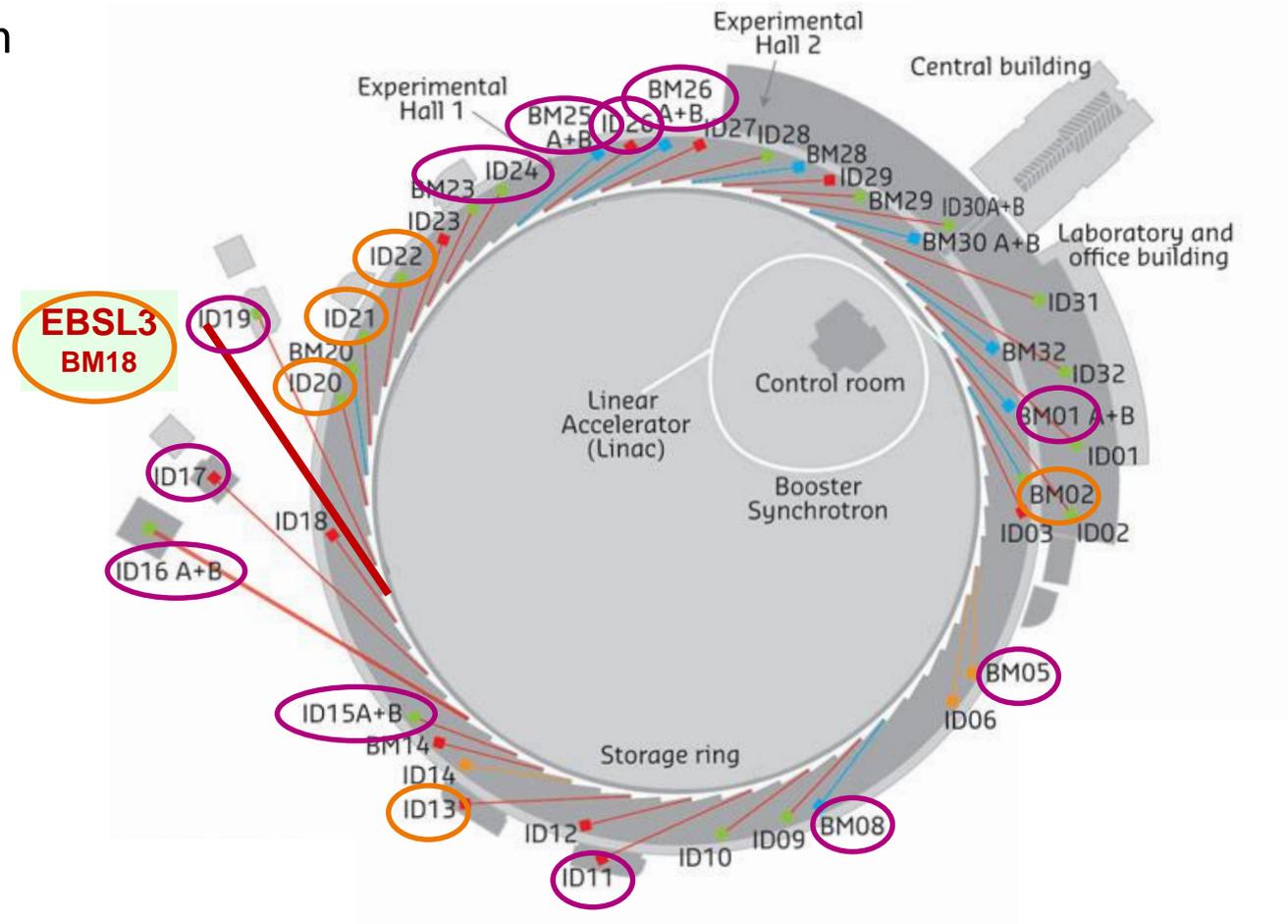


EXTREME CONDITIONS



HERITAGE AT THE ESRF

- Heritage studies via user program
- Strong in-house program



Cultural Heritage



Manufactured objects: processes during and after creation

- Evolution of technologies. Intentions of the artists/craftsmen
- Authentication
- Degradation, preservation, conservation

Natural Heritage



Non-manufactured objects: evolution of Life.

Natural processes involved at all time scales:

days-months (e.g. embryonic development)

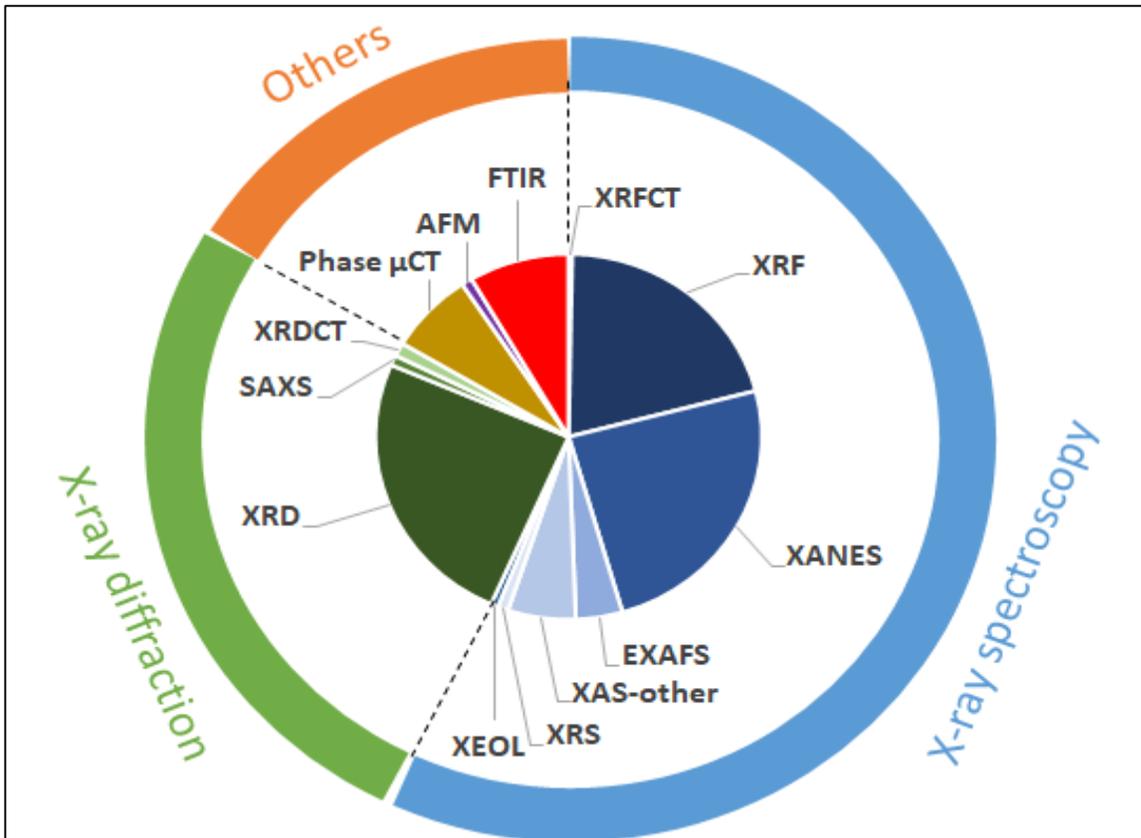
months-years (e.g. growth from child to adult)

centuries-millenia (e.g. species domestication)

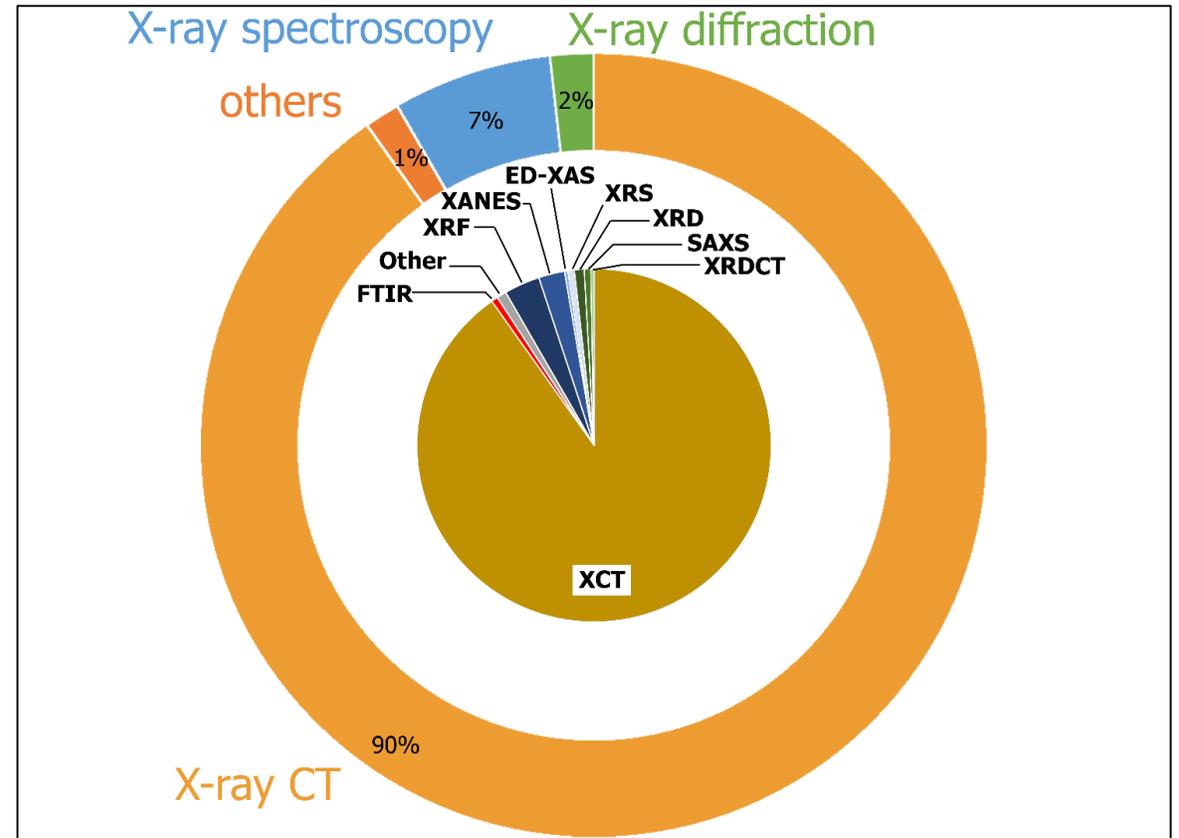
1M-1B years (life evolution)

NATURAL AND CULTURAL HERITAGE

Cultural Heritage



Natural Heritage



SOME ARTEFACTS ANALYZED AT ID21 IN 2016-2023 (NOT EXHAUSTIVE)



Inks on Papyri
Carlsberg Collection,
Copenhagen, Christiansen
Herculaneum, Brun

Cimabue's *Maestà of Santa Maria dei Servi*
(1280–1285),
L. Monico,
Perugia

Ming porcelains
Beijing Archaeological
Institute (15th-16th C.),
Ph. Sciau,
Toulouse

Ultramarine pigment in *Girl with a Pearl Earring*,
Mauritshuis, (1665),
A. Gambardella,
Amsterdam

Van Gogh's *Sunflowers*
van Gogh Museum,
(1888-1889),
L. Monico,
Perugia, Antwerp

Munch's *Scream*,
Munch Museum
(1910),
L. Monico,
Perugia

Rodin's modelling clay
Rodin museum
(1908-1913),
J. Langlois,
Paris

Miro's *Femme dans la rue*
(1973),
M. Ghirardello,
Milano

Antiquity

Today



Hellenistic Egyptian Blue
Kos, (1st C. BCE)
A. Kostomistopoulo,
Oslo

Bamiyan Buddhist paintings
Afghanistan, (6th-9th C.)
Y. Taniguchi,
Tokyo

Leonardo da Vinci's *last Supper*
Santa Maria Delle Grazie
(1495-1498)
M. Cotte,
ESRF

Rembrandt's *Night watch*
Rijksmuseum
(1642),
V. Gonzalez,
Delft

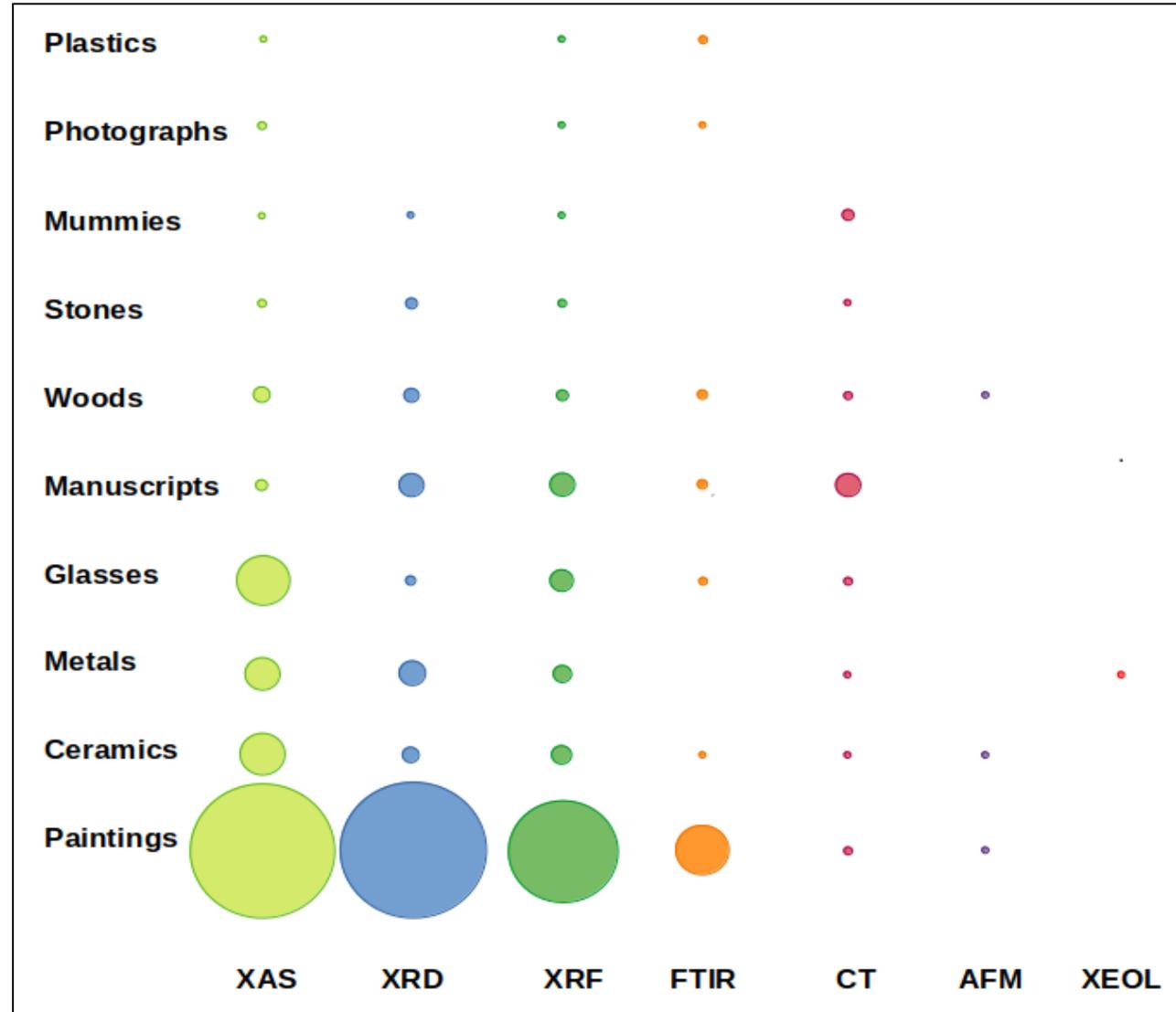
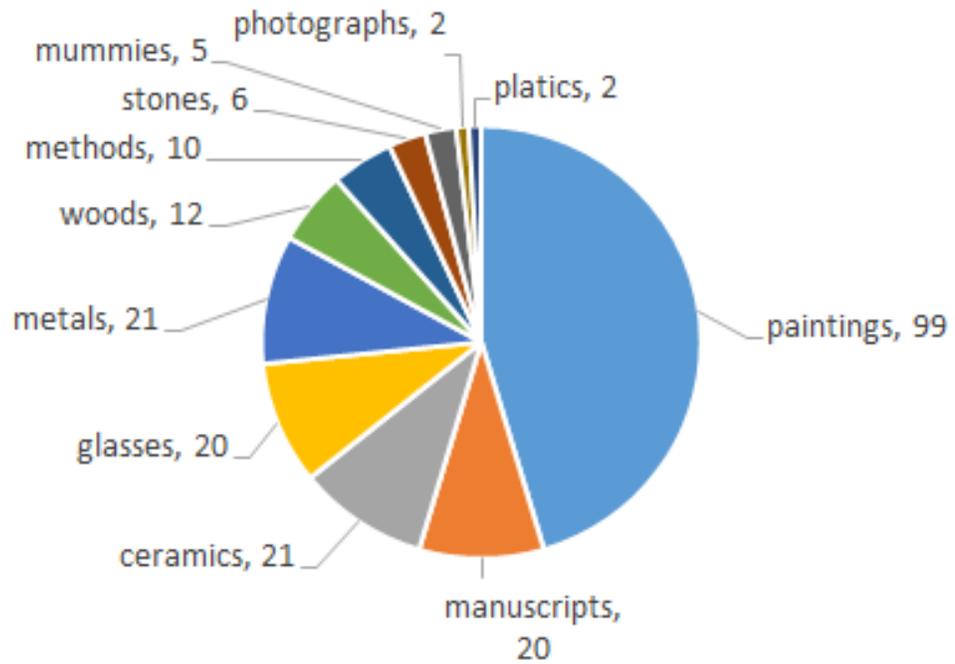
Caspar David Friedrich's *Wanderer above the Sea of Fog*
Hamburger Kunsthalle,
(1818),
I. Reiche, Paris

Porcelains, Sèvres manufacture
End 19th Beg. 20th C.
L. Verger,
Paris

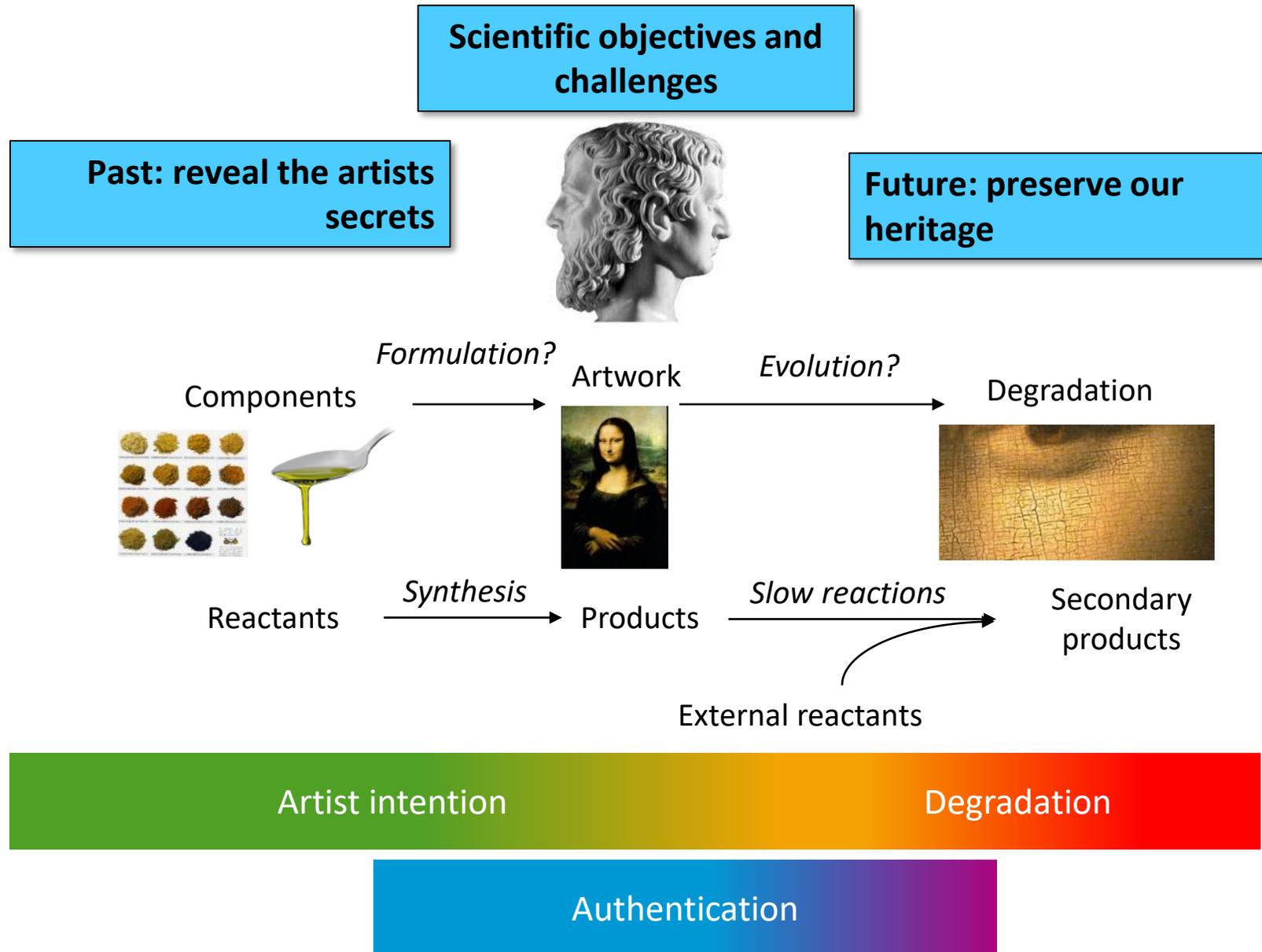
Picasso's *Femmes*
Foundation Beyeler,
(1907),
M. Ghirardello,
Milano

Ducos du Hauron early color photographs,
1870's, M. Cotte,
ESRF

WHICH TECHNIQUES TO STUDY WHICH MATERIALS?

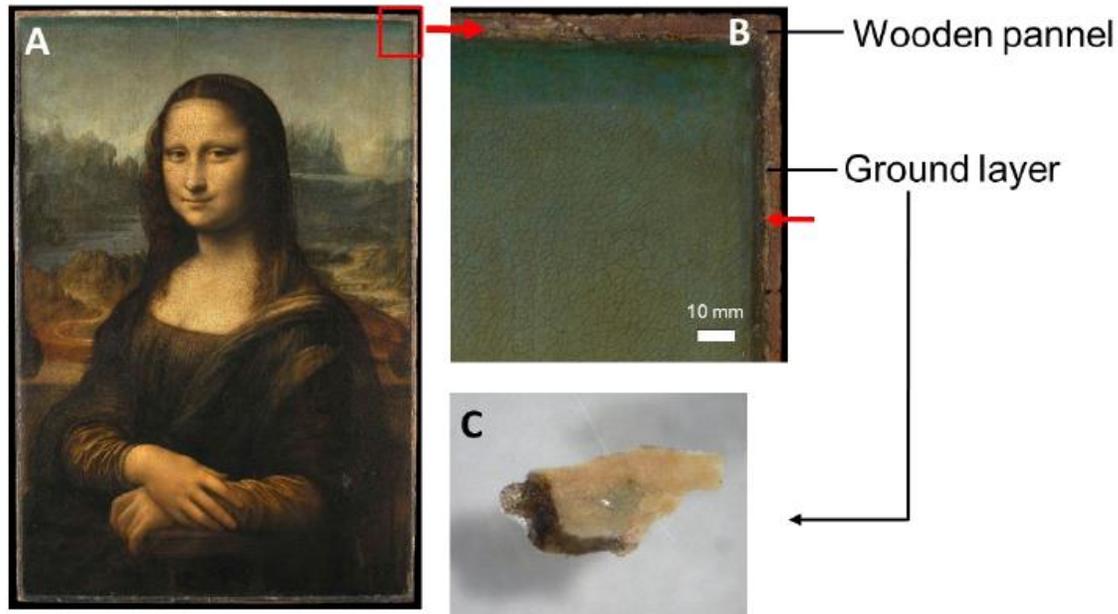


CULTURAL HERITAGE : THE MAIN SCIENTIFIC QUESTIONS

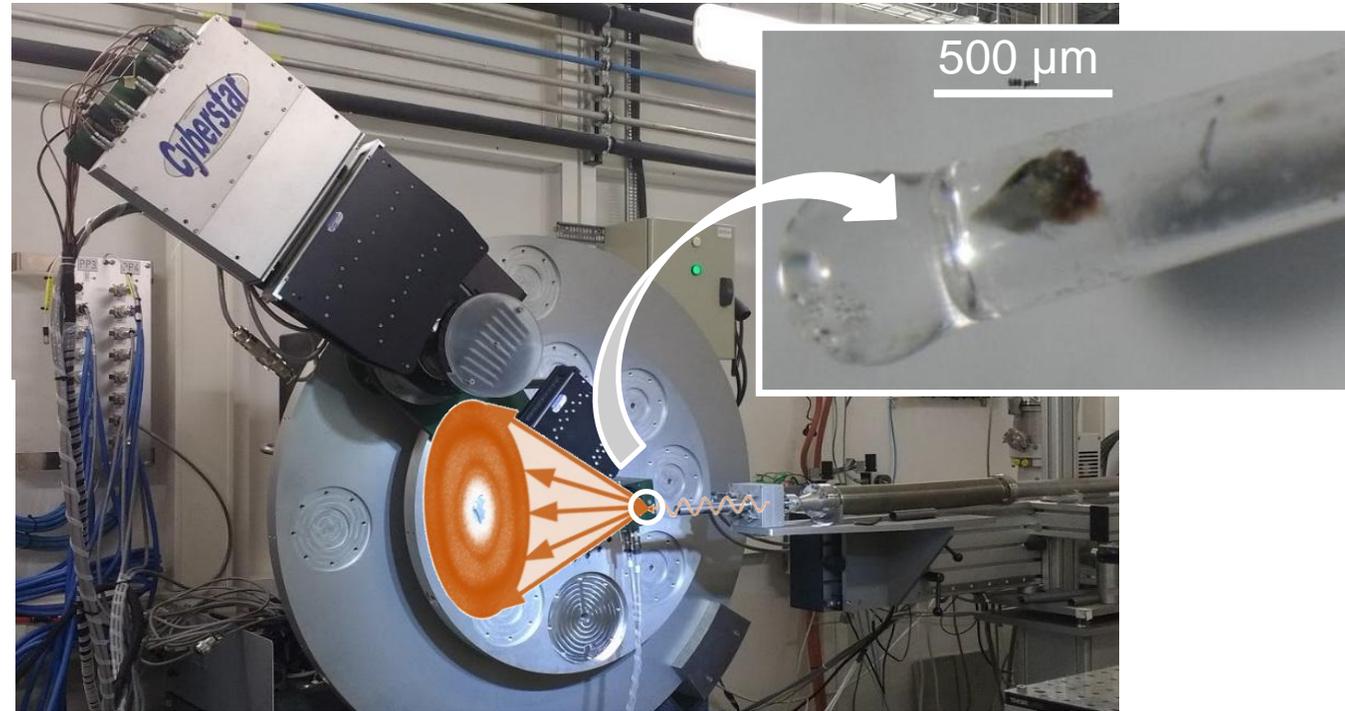


X-ray and Infrared Microanalyses of *Mona Lisa's* Ground Layer and Significance Regarding Leonardo da Vinci's Palette

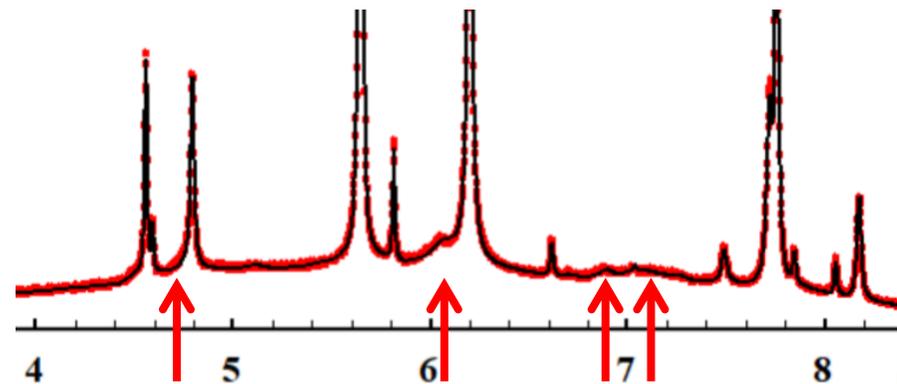
Victor Gonzalez,* Gilles Wallez, Elisabeth Ravaud, Myriam Eveno, Ida Fazlic, Tiphaine Fabris, Austin Nevin, Thomas Calligaro, Michel Menu, Vincent Delieuvin, and Marine Cotte



Detection of plumbonacrite $Pb_5(CO_3)_3O(OH)_2$, an unusual lead compound in the ground layer. Possibly formed consecutively to the reaction of oil with the PbO drier.



High angular resolution X-ray powder diffraction, ID22, ESRF, A. Fitch and C. Dejoie



High signal to noise ratio

Instrumental broadening (FWHM of Si (111) peak): $\sim 0.0027^\circ$

DA VINCI'S PAINTING MATERIAL CONFIRMED BY MICRO-X RAY POWDER DIFFRACTION (ID13)

J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JACS

Article

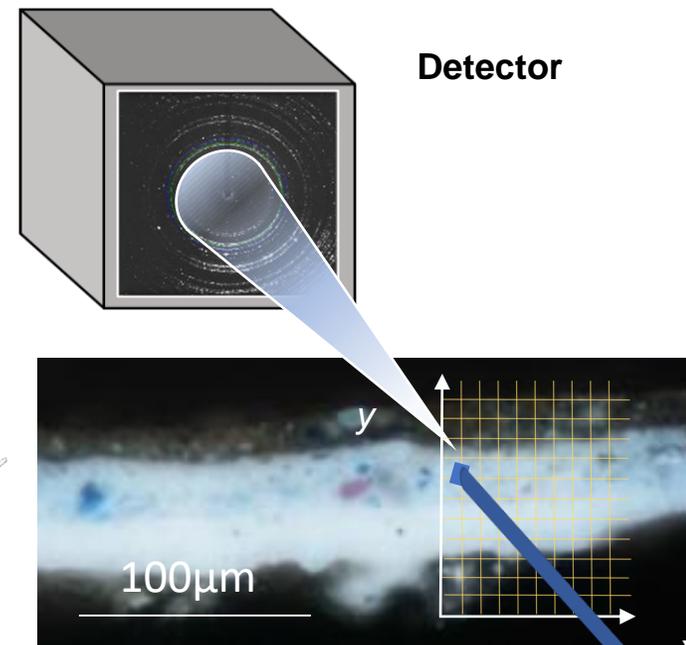
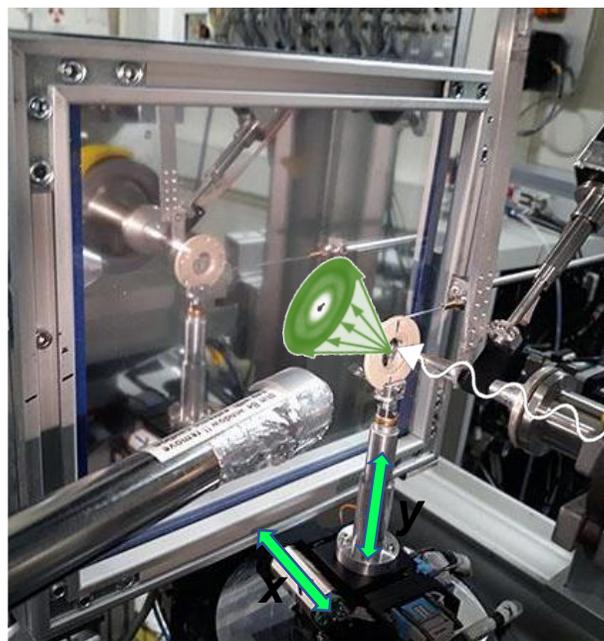
X-ray and Infrared Microanalyses of *Mona Lisa's* Ground Layer and Significance Regarding Leonardo da Vinci's Palette

Victor Gonzalez,* Gilles Wallez, Elisabeth Ravaud, Myriam Eveno, Ida Fazlic, Tiphaine Fabris, Austin Nevin, Thomas Calligaro, Michel Menu, Vincent Delieuvin, and Marine Cotte

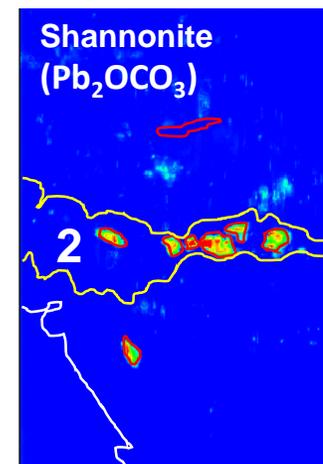
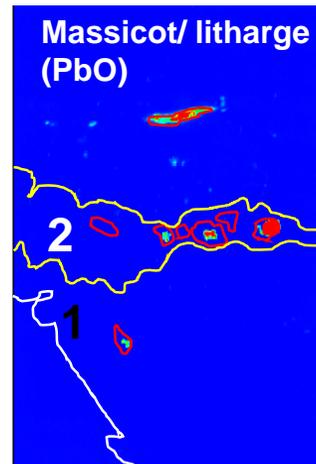
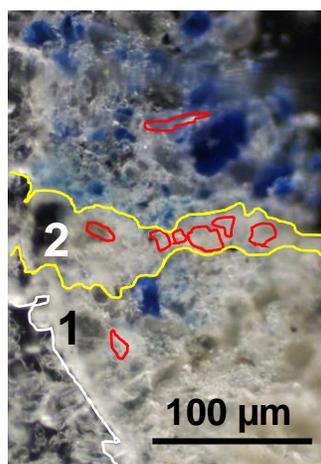


Detection of PbO, plumbonacrite but also, shannonite, Pb_2OCO_3 , another unusual, lead oxycarbonate.

Confirming the use of PbO by Leonardo *da Vinci* in his paintings.



Micro X-ray diffraction mapping, ID13, ESRF, M. Burghammer



Beam size $2 \times 2 \mu m^2$

Map size $200 \times 300 \mu m^2$

15ms/ pixel

XRF collected simultaneously to XRD

Degradation Process of Lead Chromate pigments in Van Gogh's paintings



Identifying lead chromate pigments in Van Gogh paintings in particular with portable instruments

Characterizing the photo-sensitivity of model lead chromate pigments and proposing a risk assessment of color modification in paintings

Letizia Monico,

Koen Janssens, Brunetto Brunetti, Costanza Miliani (and many others)

Centre SMAArt and Dipartimento di Chimica, Università degli Studi di Perugia, Perugia, Italy.

Department of Chemistry, University of Antwerp, Belgium

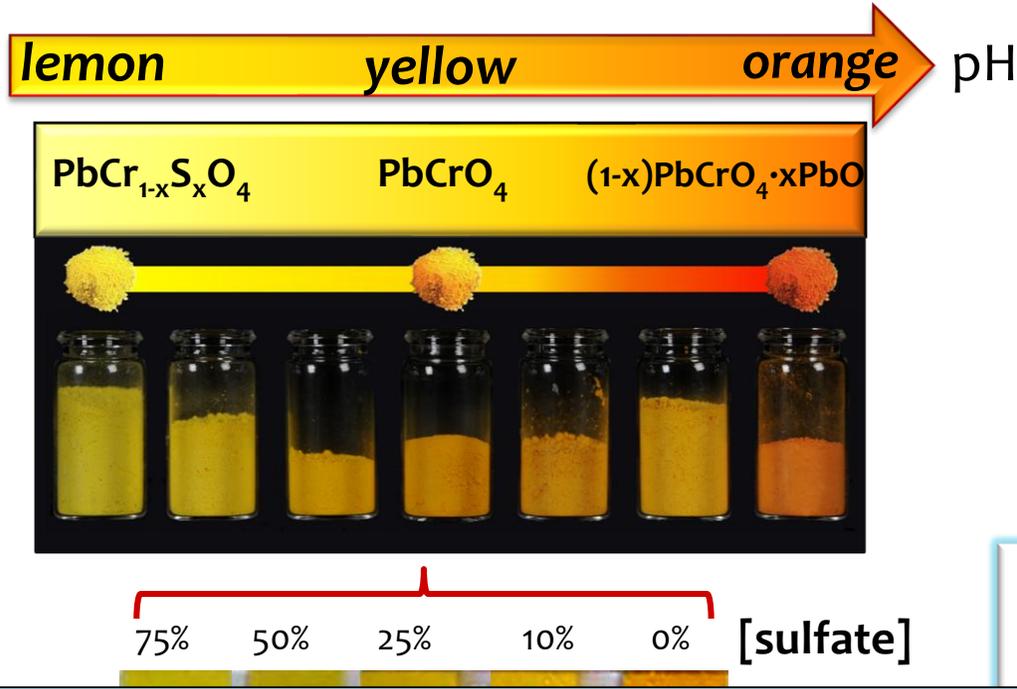
DEGRADATION OF CHROME YELLOWS IN SUNFLOWERS



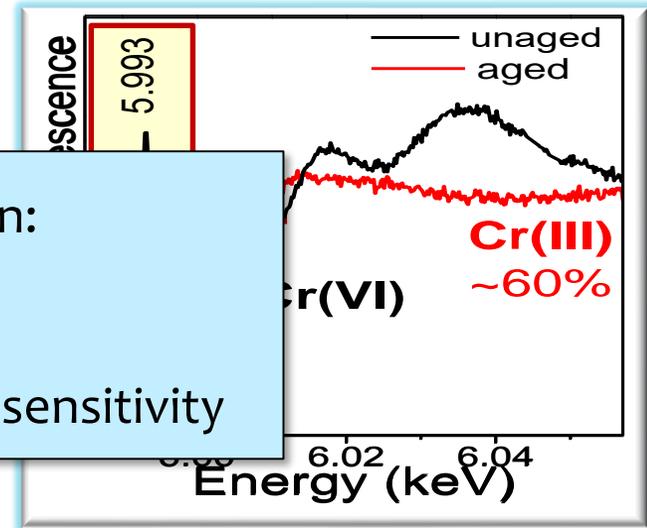
Letter from Vincent van Gogh to his brother Théo, 11 Avril, 1888

...
côté de les avoir aussi et de cette façon
il n'y a pas d'imprudences
Tu as eu raison de dire à Tardet qu'il fallait
ajouter la laque généralement le plus de même
il l'a envoyé je veux de vérifier - toutes
les couleurs qui à l'impressionisme ont
mises à la mode sont chargées de couleurs
de plus de les employer hardiment trop
chères de temps les avancera que trop
sans doute la commande que j'ai faite
soit les 3 chromes (l'orange le jaune
le citron) le bleu de Prusse l'émerald
les laques de jaunes de la verte
tout cela se trouve guère sur la palette
hollandaise mais orange et jaune -
seulement cela se trouvait sur celle
de Sébastien qui avait la rage des
deux couleurs les plus condamnées et trop
pour les meilleures raisons le citron et
le bleu de Prusse - Cependant il me semble
qu'il en me fait de superbes avec cela des
bleus et des jaunes citrons. Pour ceux
de main à toi à l'usage et encore moi
j'ai bien aimé des couleurs la L. Vercell-t

DIFFERENT CHROME YELLOWS AGE DIFFERENTLY



Cr K-edge X-ray absorption spectroscopy at ID21



Colour change is linked to a modification of Cr speciation:
reduction of Cr(VI) into Cr(III)

Higher the sulfate proportion, higher the solubility and the light sensitivity

Technical challenge

- Large corpus of model samples to assess many parameters

Thicket, K. Janssens, W. De Nolf, C. Miliani, J. Verbeeck, H. Tian, H. Tan, J. Dik, M. Radepont and M. Cotte, "Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Synchrotron X-ray Spectromicroscopy and Related Methods. 1. Artificially Aged Model Samples", *Analytical Chemistry*, 83, 1214-1223 (2011). And following publications (*Anal Chem*, *JAAS*, *Angew. Chemie*)

ANALYSE OF THE SUNFLOWERS BY RAMAN, REFLECTION MID-FTIR

Yellow-orange
 $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$

Orange
Lightfast
Chrome orange
($\text{PbCrO}_4 \cdot \text{PbO}$)

Light yellow
Light-sensitive
 $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ($x \sim 0.5$)



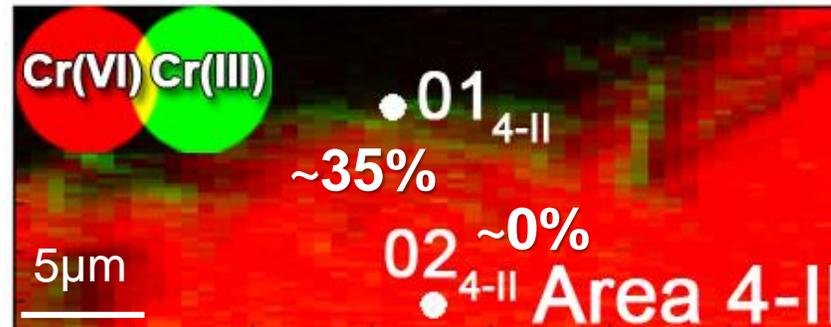
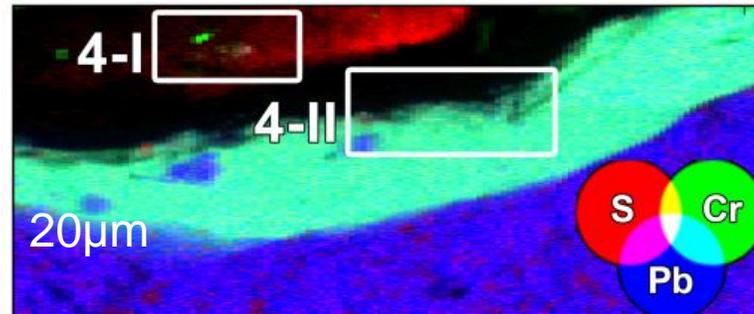
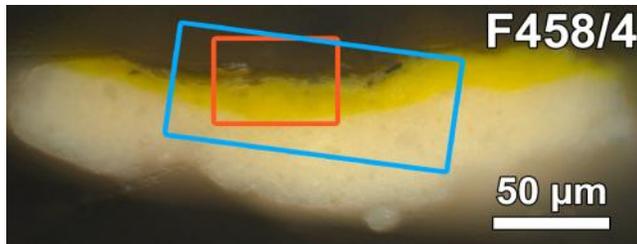
Background
Light-sensitive
 $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ($x \sim 0.5$)

Ocre yellow
 PbCrO_4 (stable)
 $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ($x \sim 0.5$)
(light-sensible)

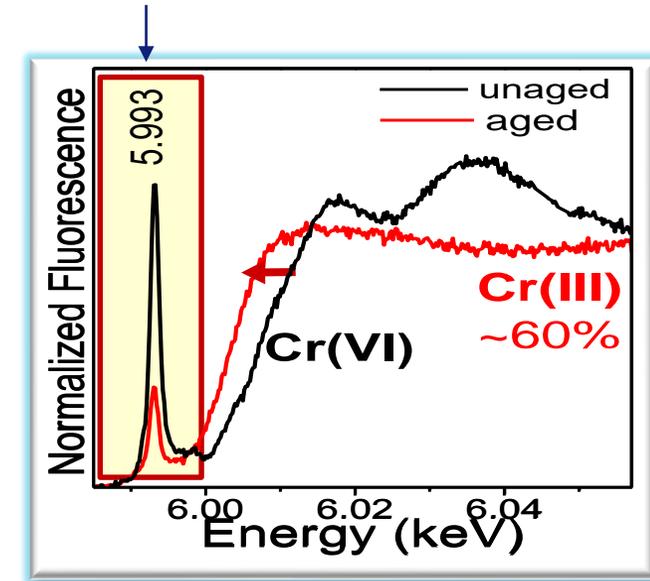
Ocre vermilion
Light sensitive
 $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ($x \sim 0.5$)

Table
Light sensitive
 $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ($x \sim 0.5$)

SYNCHROTRON MICRO-XAS ANALYSIS OF A FRAGMENT FROM THE TABLE (ID21)



At this energy, over-excitation of Cr(VI)



Technical challenges:

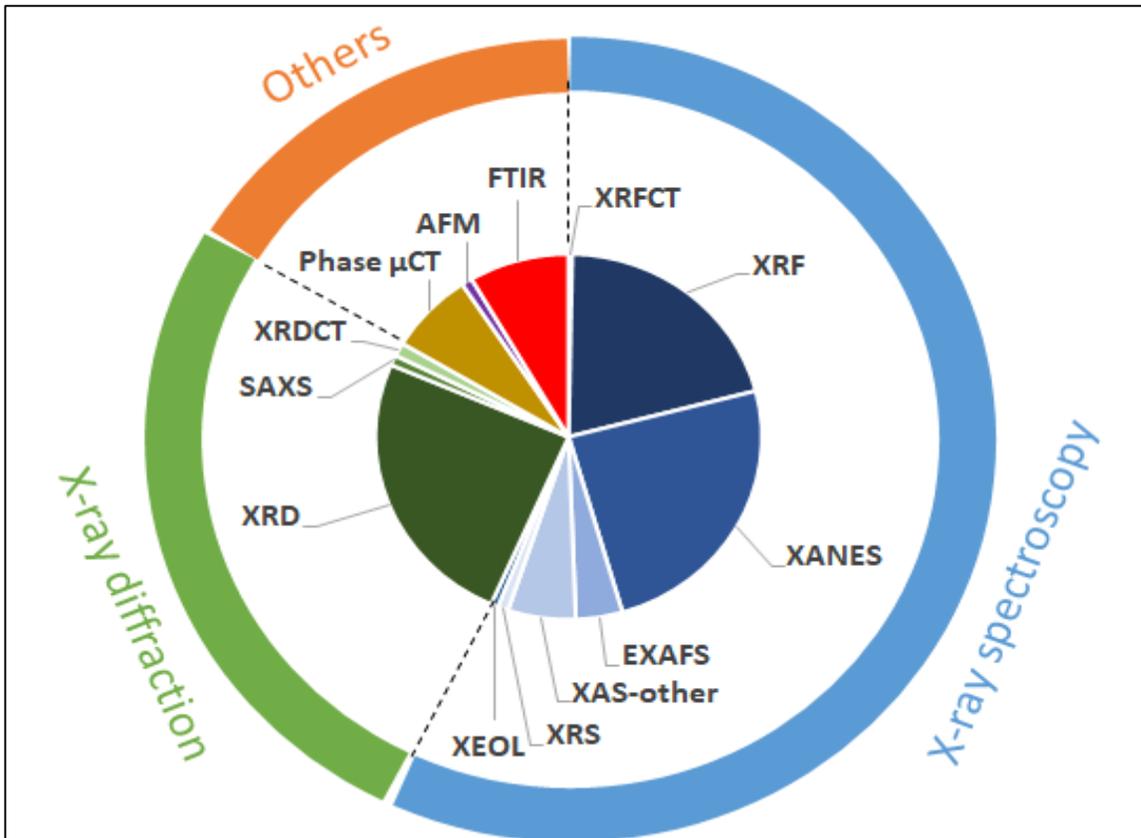
- Very thin degradation layer
- Main elemental composition constant
- Degradation products can be amorphous

There is indeed degradation of chrome yellow in the Sunflowers (table) with chromate reduction, but this is very superficial (<1μm)

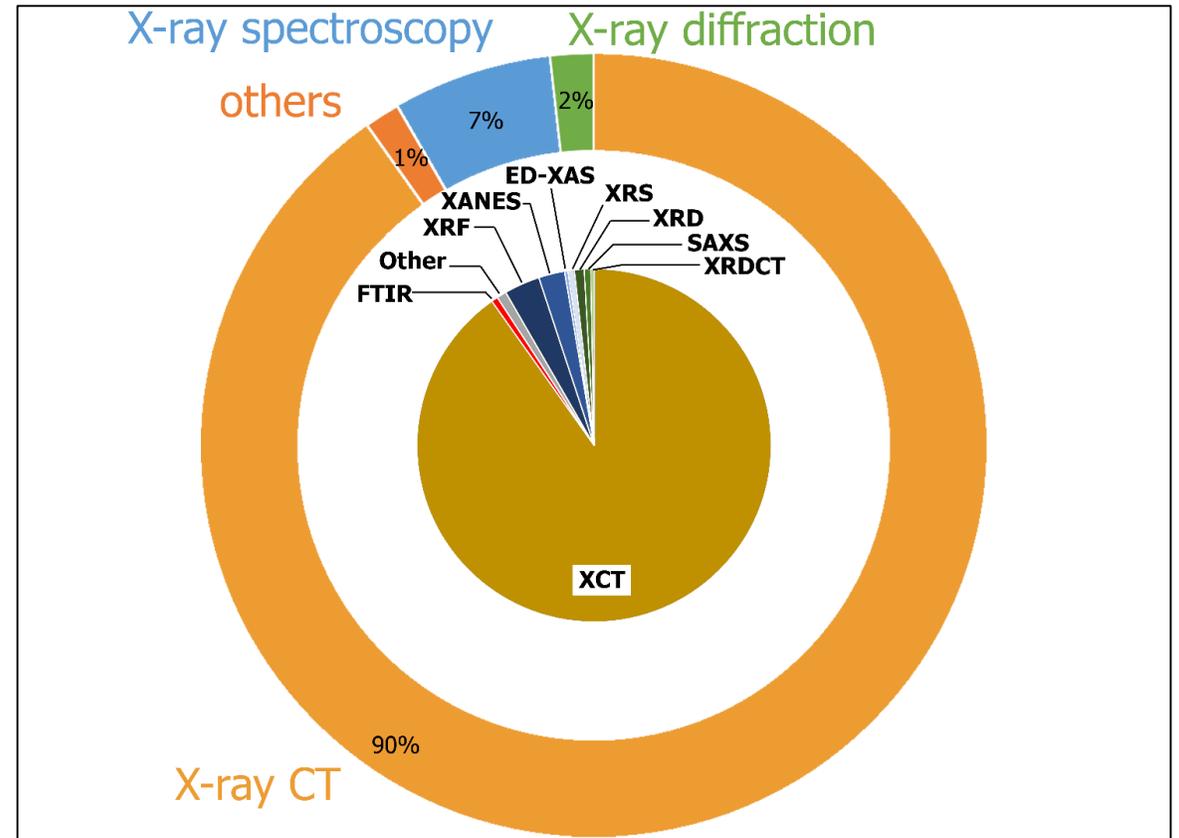
E. Hendriks, F. Vanmeert, G. Van der Snickt, M. Cotte, G. Falkenberg, B. G. Brunetti and C. Miliani, "Evidence for Degradation of the Chrome Yellows in Van Gogh's Sunflowers: A Study Using Noninvasive In Situ Methods and Synchrotron-Radiation-Based X-ray Techniques", *Angewandte Chemie*, 127, 14129-14133 (2015).

NATURAL AND CULTURAL HERITAGE

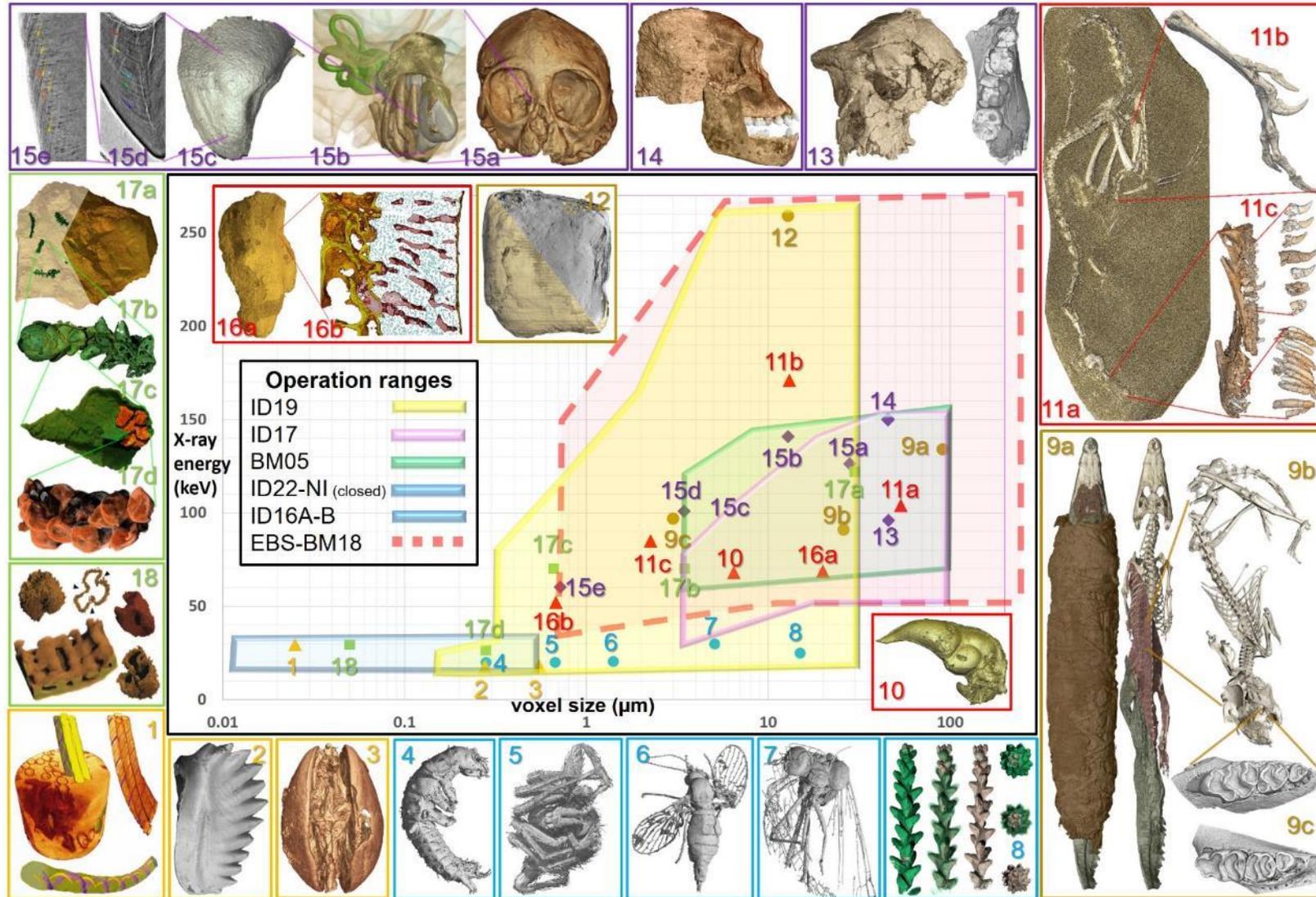
Cultural Heritage



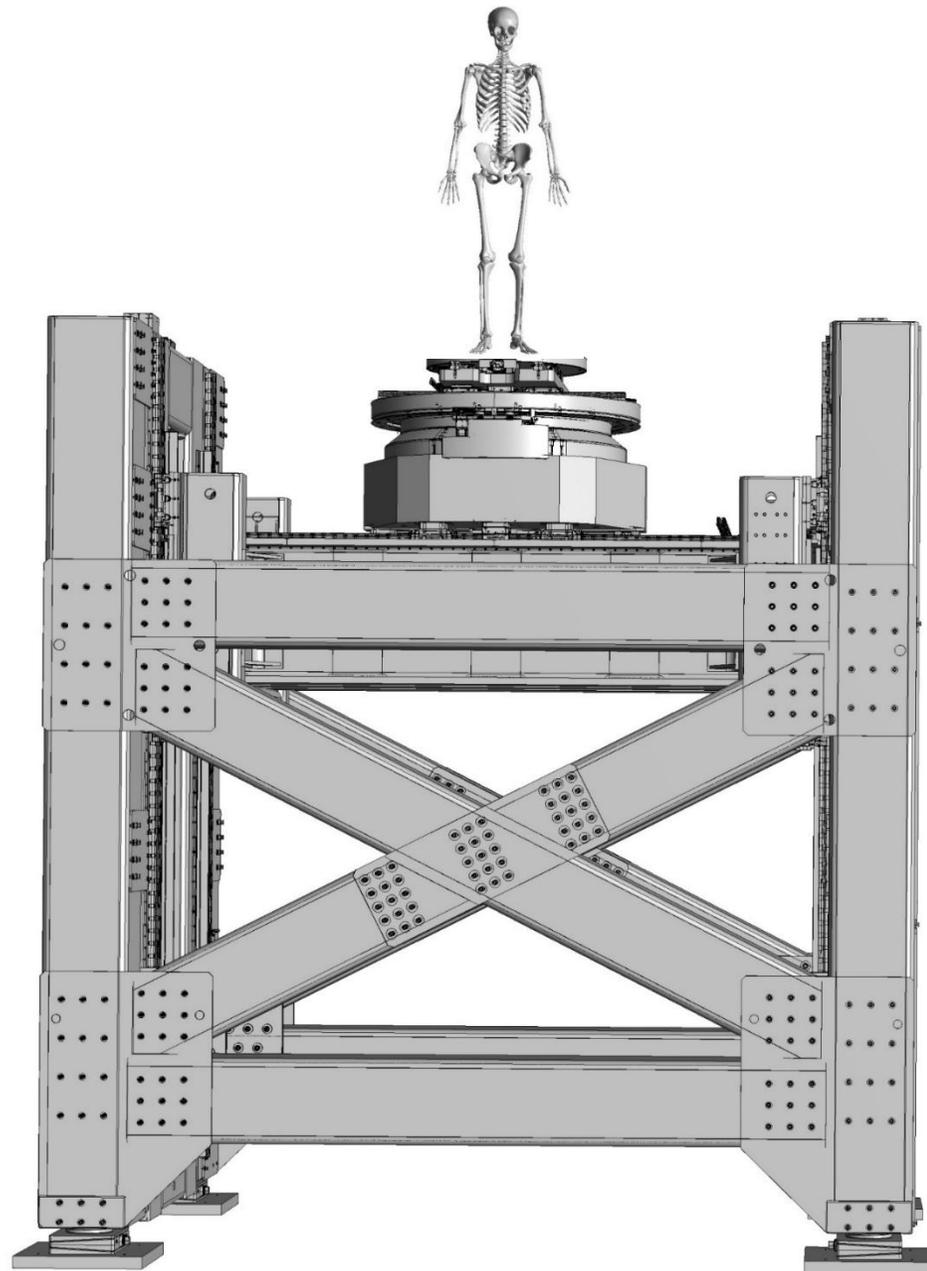
Natural Heritage



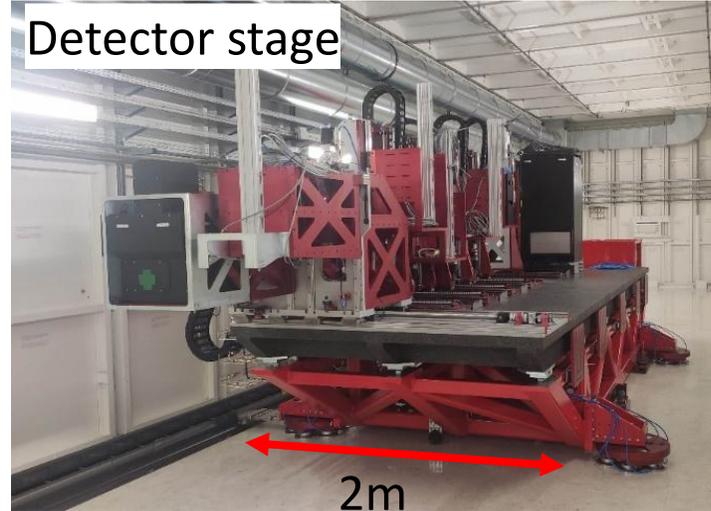
PHASE CONTRAST TOMOGRAPHY FOR PALEONTOLOGY AND ARCHAEOLOGY



THE BM18 BEAMLINE



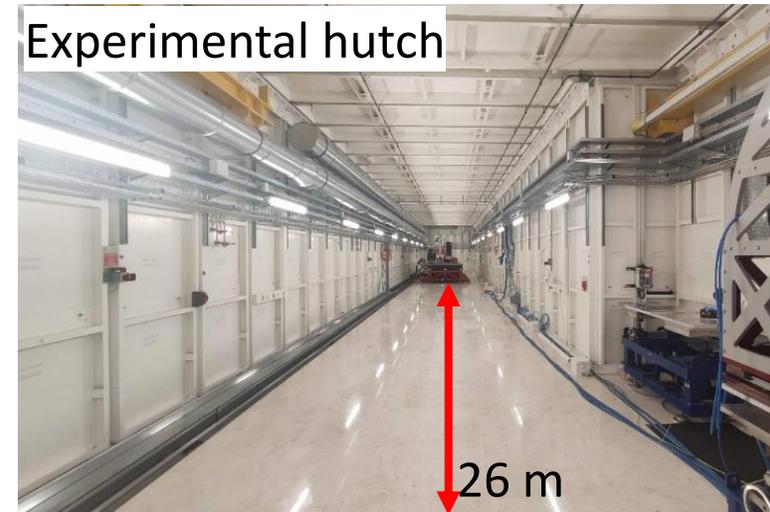
Detector stage



Versatile Multi resolution detector stage:
almost continuous pixel size
from $0.7 \mu\text{m}$ to $\sim 90 \mu\text{m}$

Sample stage
designed to mount
samples up to
250 cm height and
300 kg weight

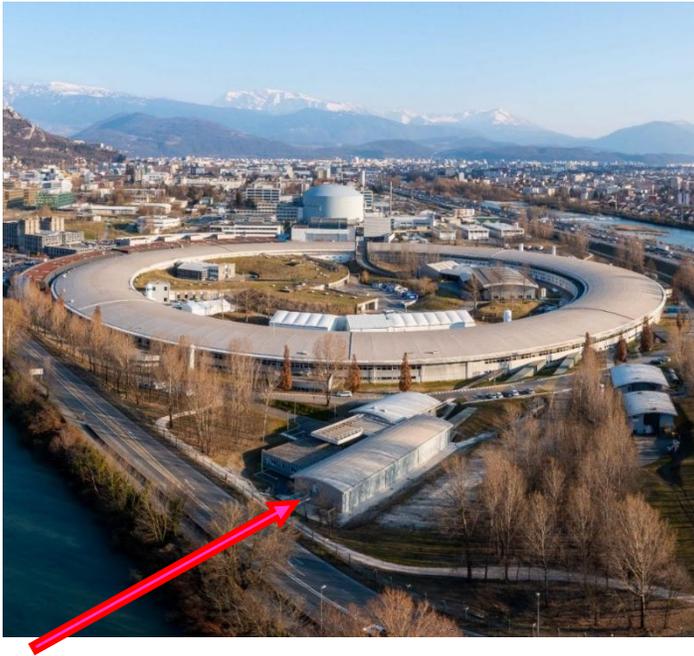
Experimental hutch



Contact: vincent.fernandez@esrf.fr

BM18 BEAMLINE FOR HIERARCHICAL PHASE-CONTRAST TOMOGRAPHY

Beamline fully optimized for hierarchical (voxel from 90 to $0.7\mu\text{m}$) phase contrast tomography of large (up to 2m) and heavy (up to 300kg) objects

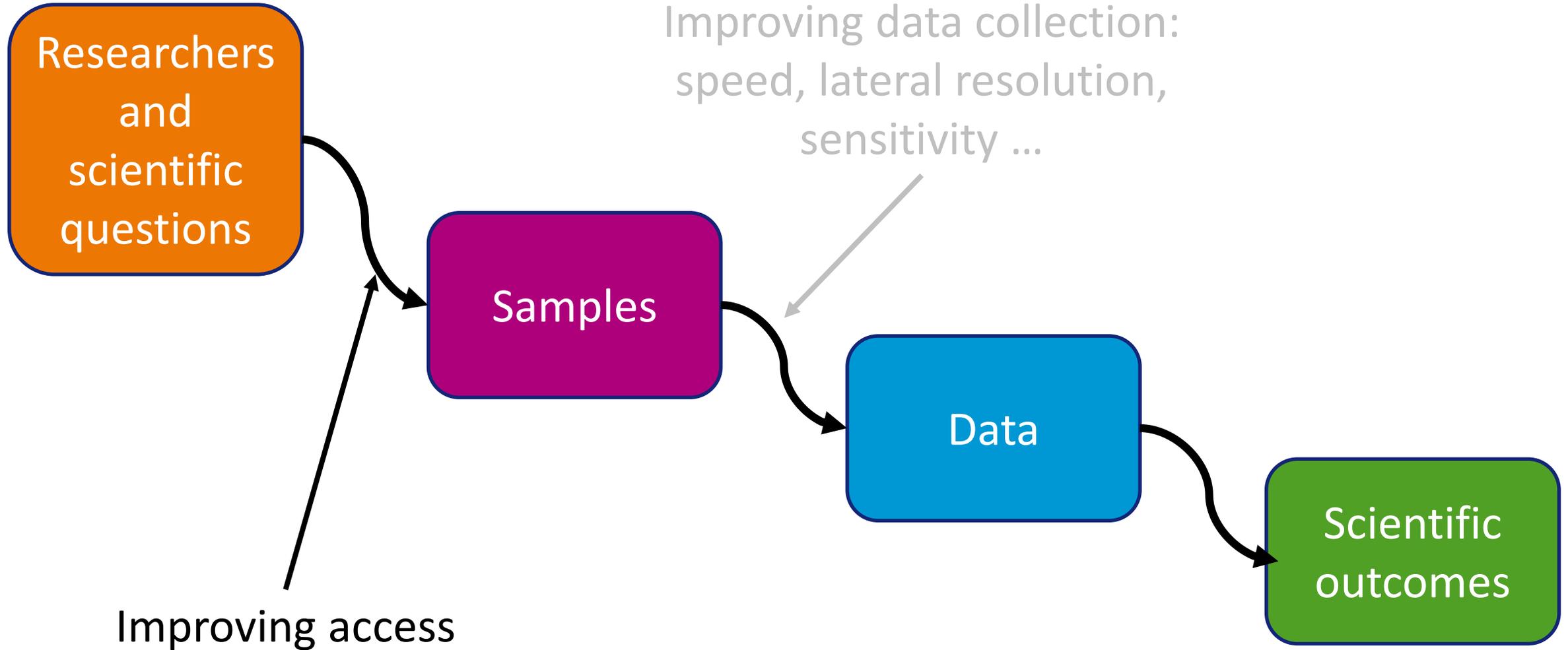


Violin imaged on BM18 using a voxel size of $33\mu\text{m}$, at 180 keV, in ~2h



Courtesy Paolasini, Tafforeau

STEPS ALONG THE RESEARCH PATH AND IMPACT OF THE ESRF UPGRADE



GETTING BEAMTIME AT A SYNCHROTRON FACILITY: THE PEER-REVIEW PROCESS

Idea



2-page proposal

01/03
10/09

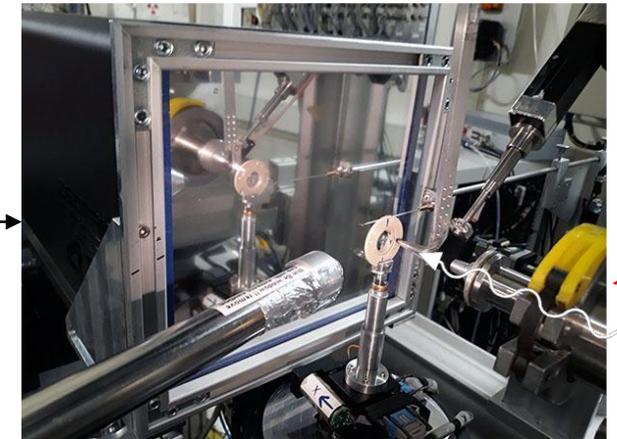
Peer-review process:
scientific excellence

Monthly planner

MONTH: _____		YEAR: _____				
MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	SATURDAY	SUNDAY
<input type="checkbox"/>						
<input type="checkbox"/>						
<input type="checkbox"/>						

From 1 to 6 days
24/24

Beamtime ESRF!



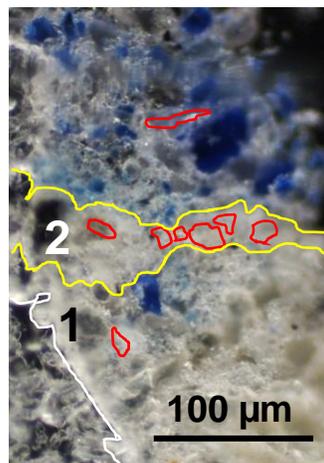
X-rays

High tech instruments

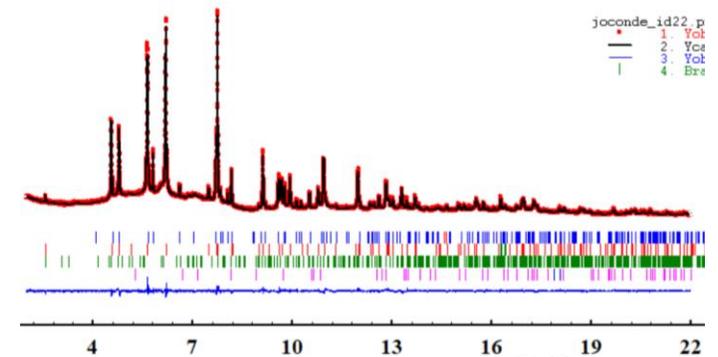
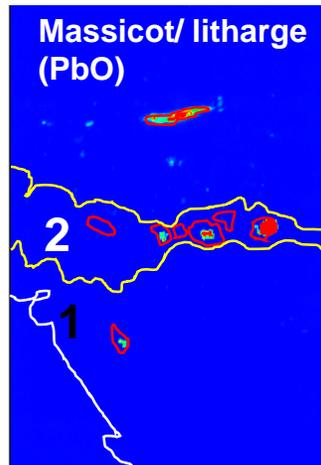
Next deadline: 10 Sept



How to make the access to the ESRF easier,
in particular when users need only few hours of beamtime?

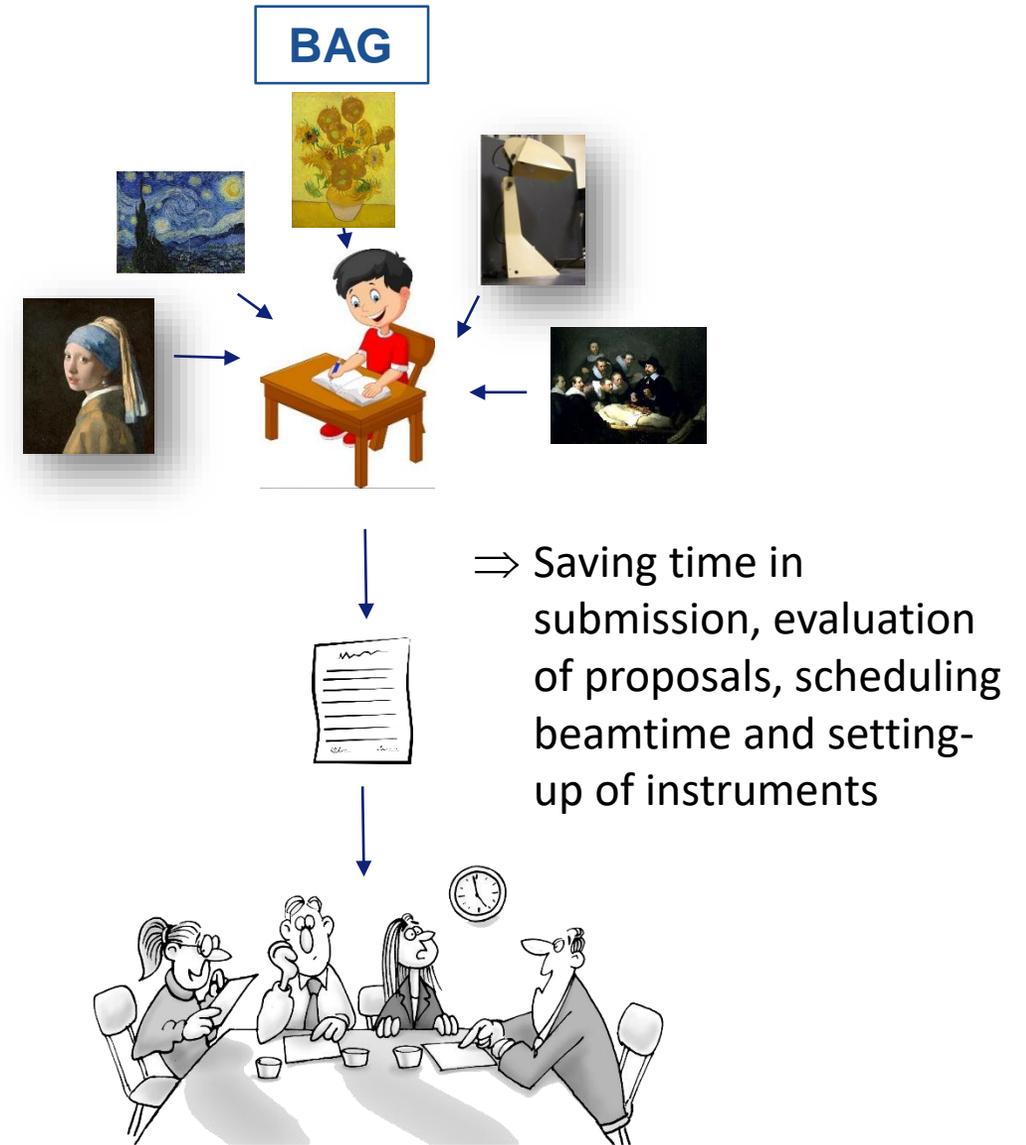
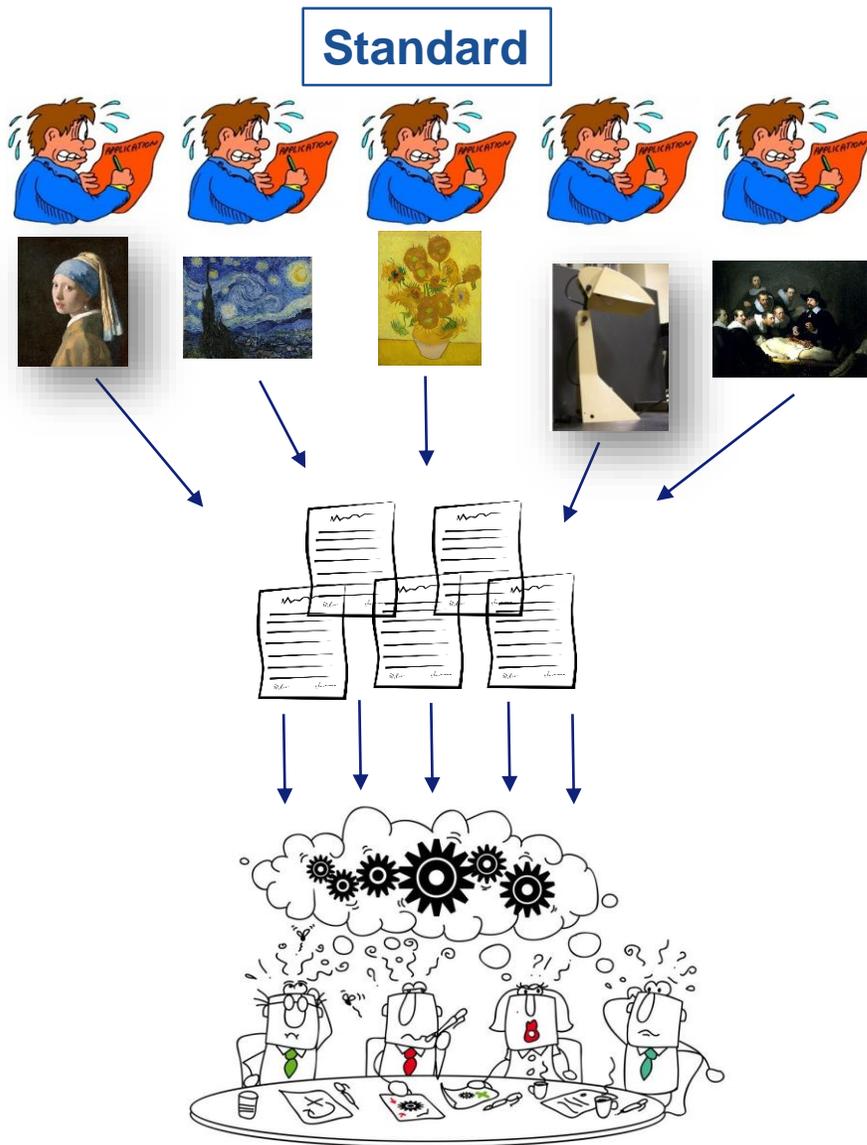


1 map at ID13 ~20'



1 HR-XRPD at ID22 ~1-2h

FROM STANDARD ACCESS MODELS TO BLOCK ALLOCATION GROUP (BAG) ACCESS



THE “HISTORICAL MATERIALS” BLOCK ALLOCATION GROUP: A NEW SHARED ACCESS



RIJKS MUSEUM



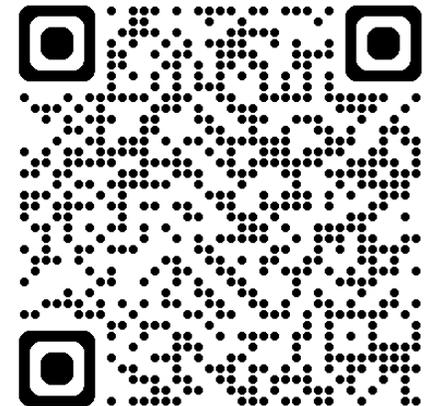
POLITECNICO MILANO 1863



<https://www.esrf.fr/BAG/HG172>

Heritage-bag@esrf.fr

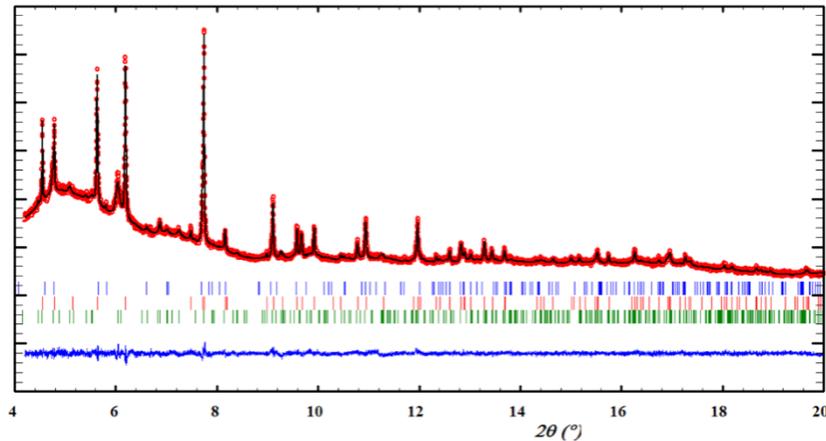
- 13 European teams + Metropolitan Museum
- ESRF: **C. Holé**, M. Cotte, G. Robertson
- ENS Paris-Saclay (former Rijksmuseum): **V. Gonzalez**
- Rijksmuseum (ex University of Antwerp, KIKIRPA): **F. Vanmeert**
- CNR-SCITEC: **L. Monico**
- Courtauld Institute of Art: **A. Burnstock**
- Politecnico di Milano: **D. Comelli**
- Rijksmuseum: **K. Keune**
- IRCP/C2RMF: **I. Reiche**
- Metropolitan Museum (ex University of Cambridge): **E. Purdy**
- Universitat Politècnica de Catalunya: **N. Jiménez**
- IRCP: **G. Wallez**
- TU Delft: **M. Alfeld**
- ISPC-CNR: **A. Suzuki**
- AXES: **K. Janssens**



ID22 : High-angular resolution XRD

- Energy: ~35 keV
- Scan range 2θ : 3 – 20°
- Analysis time: ~20 min/powder; ~2 h/historical sample
- Instrumental function 2θ (FWHM of (111) Si peak) ~ 0.0027°
- Samples in capillaries

⇒ precise and sensitive detection of crystalline phases, their identification, and the characterization of their microstructural and structural properties



3 days every 6 months
Local contact : Catherine Dejoie



ID13 : High-lateral resolution XRD

- Energy: ~13 keV
- Analysis time: ~10 min -2 h/map (15ms/ pixel)
- Beam size ~ 2×2μm²
- Samples as thin sections (preferable) or cross-sections

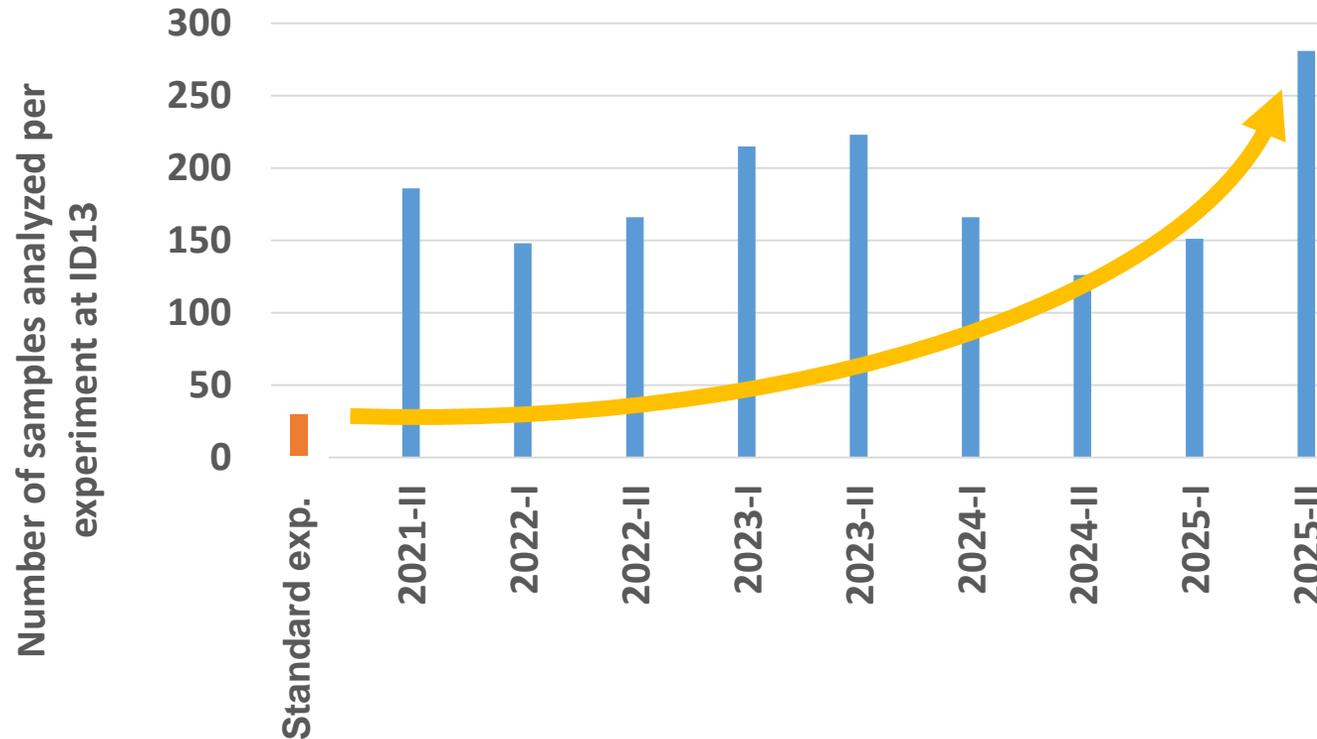
⇒ stratigraphical distribution of crystalline phases at the micrometer scale



- Sphalerite (ZnS)
- Lead titanate (PbTiO₃)
- Rutile (TiO₂)
- Zincite (ZnO)
- Hydrocerussite (Pb₃(CO₃)₂(OH)₂)
- Anglesite (PbSO₄)
- Barite (BaSO₄)
- Cerussite (PbCO₃)
- Gypsum (CaSO₄·2H₂O)
- Calcite (CaCO₃)

4 days every 6 months
Local contact : Georgina Robertson

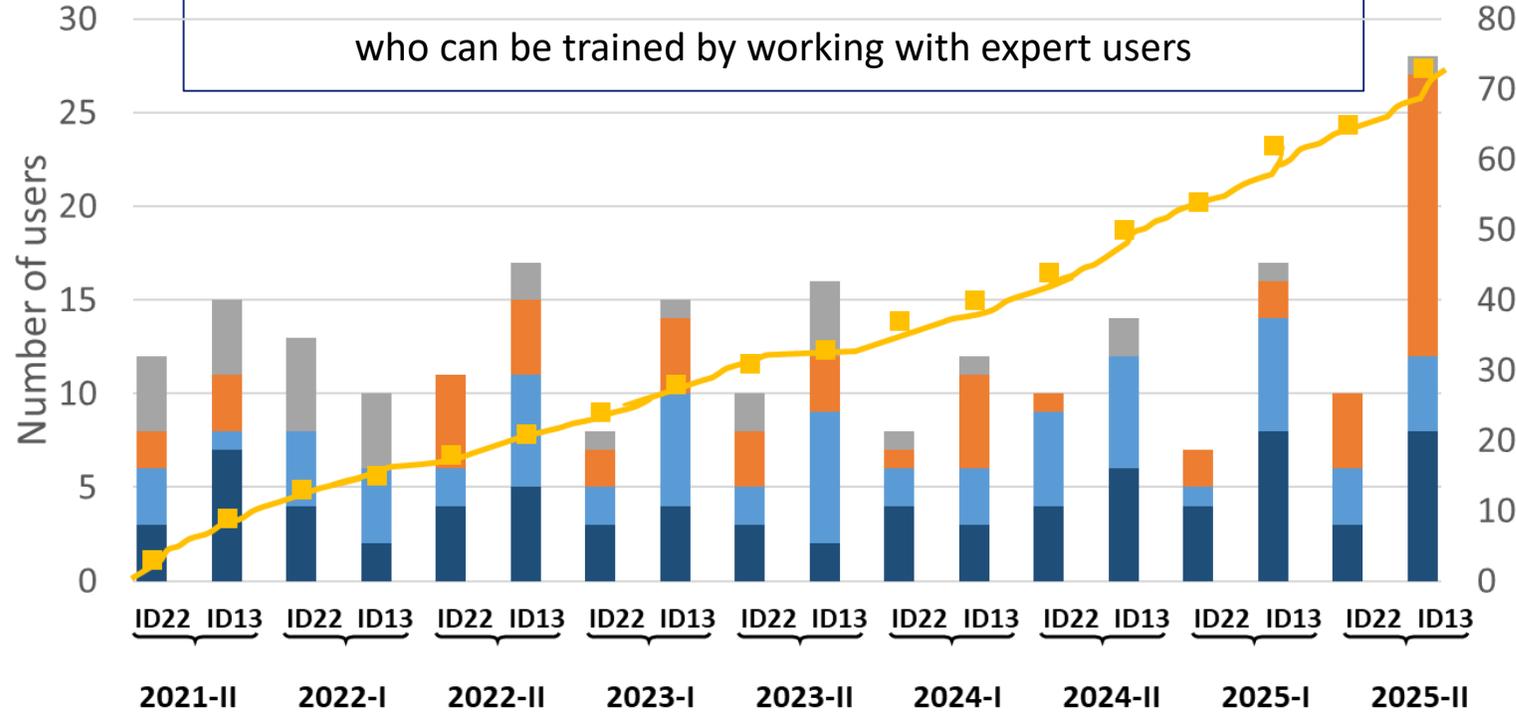
Already more than 2500 artistic fragments analyzed



Thanks to the Historical Materials BAG access, **we have boosted the speed of data acquisition and the number of analyzed samples.**

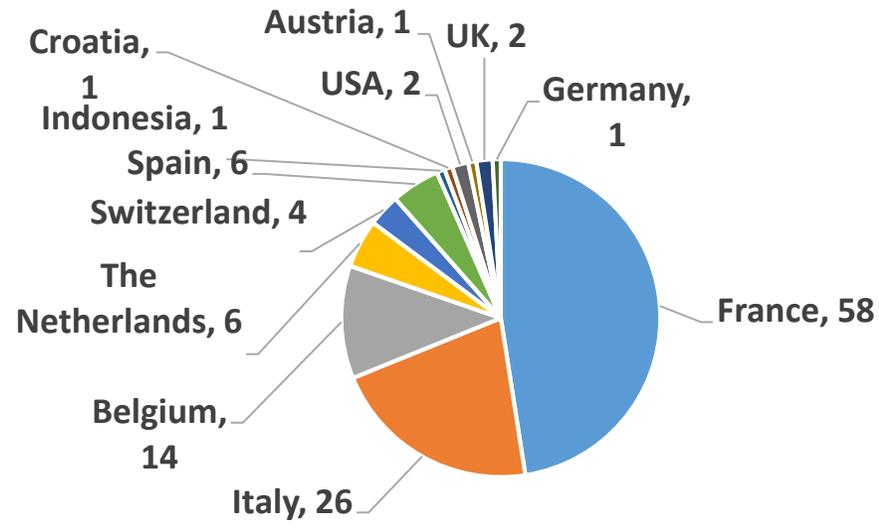
THE "HISTORICAL MATERIALS" BLOCK ALLOCATION GROUP: A VERY EFFICIENT WAY TO TRAIN NEW USERS

BAG gives an easy access to beamtime, in particular to **new users**, who can be trained by working with expert users



- end-users
- experienced on-site users
- cumulative number of first-time on-site user
- remote users
- first time on-site users

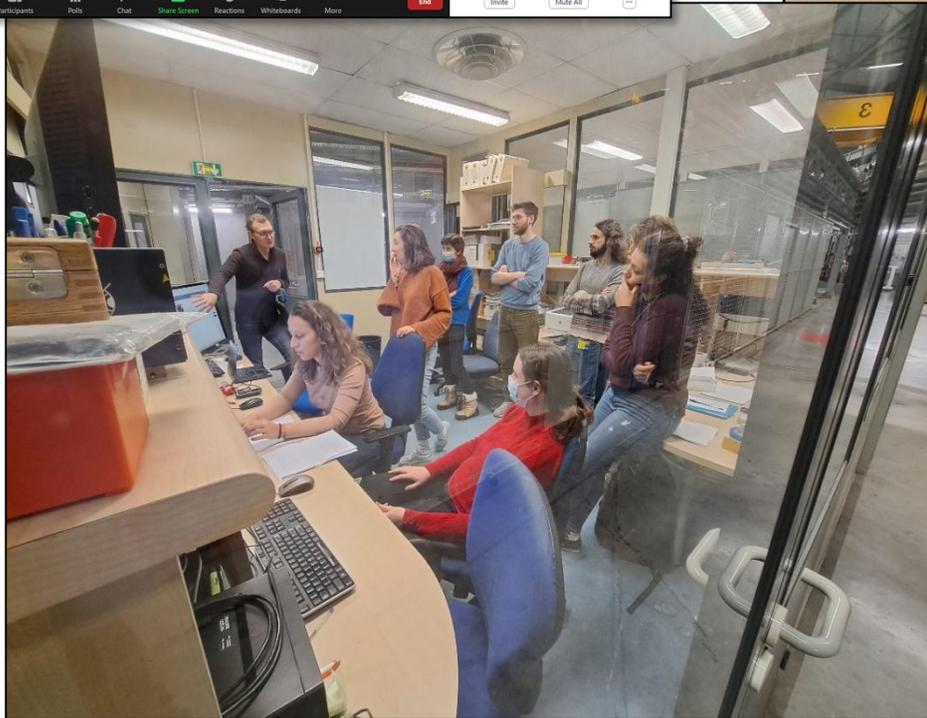
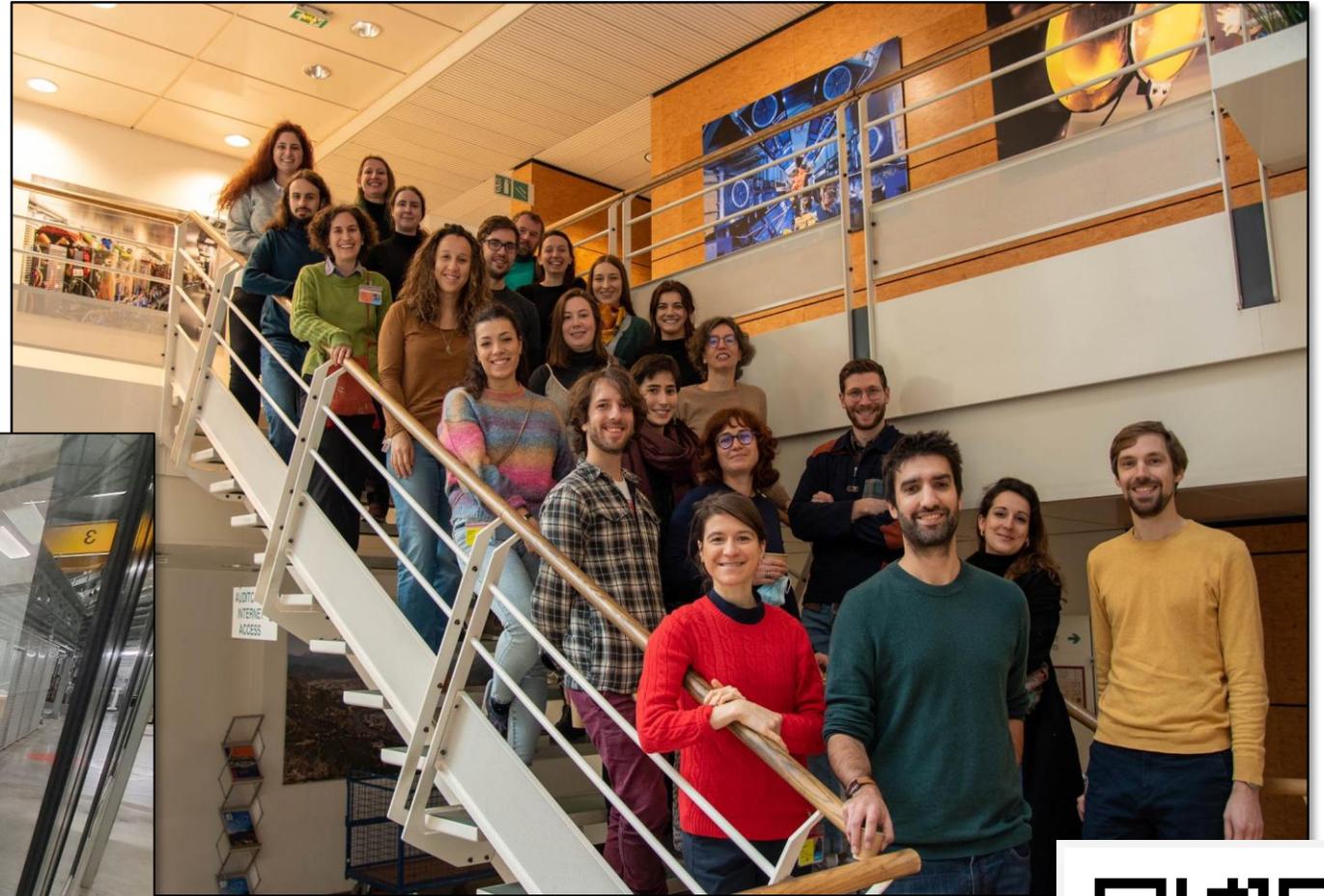
Cumulative number of new users on site



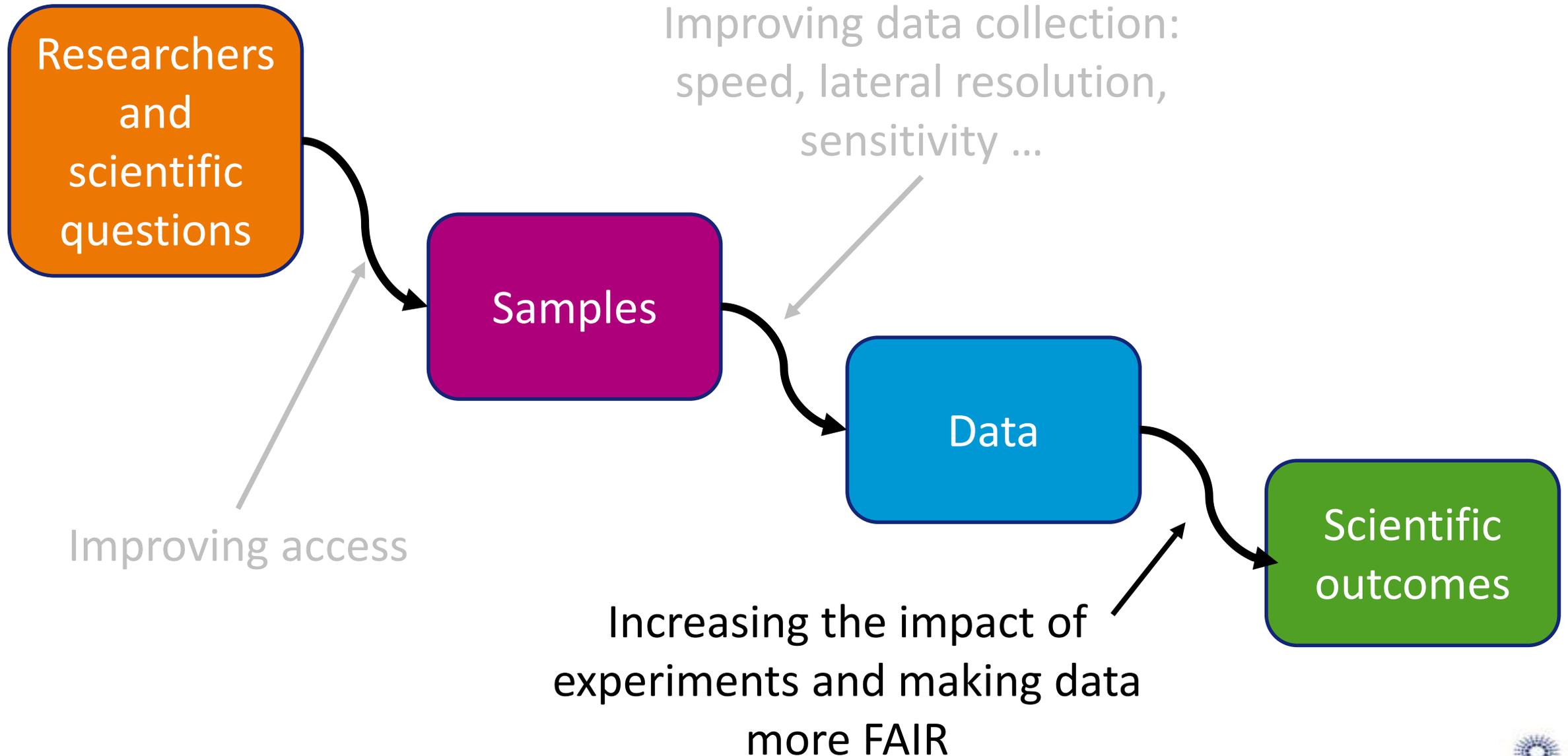
Around 13 users per experiment
 Already 70 first time on-site users in 3.5 years
 A total of 106 users (on-site, remote, end-user)
 A total number of 151 partners



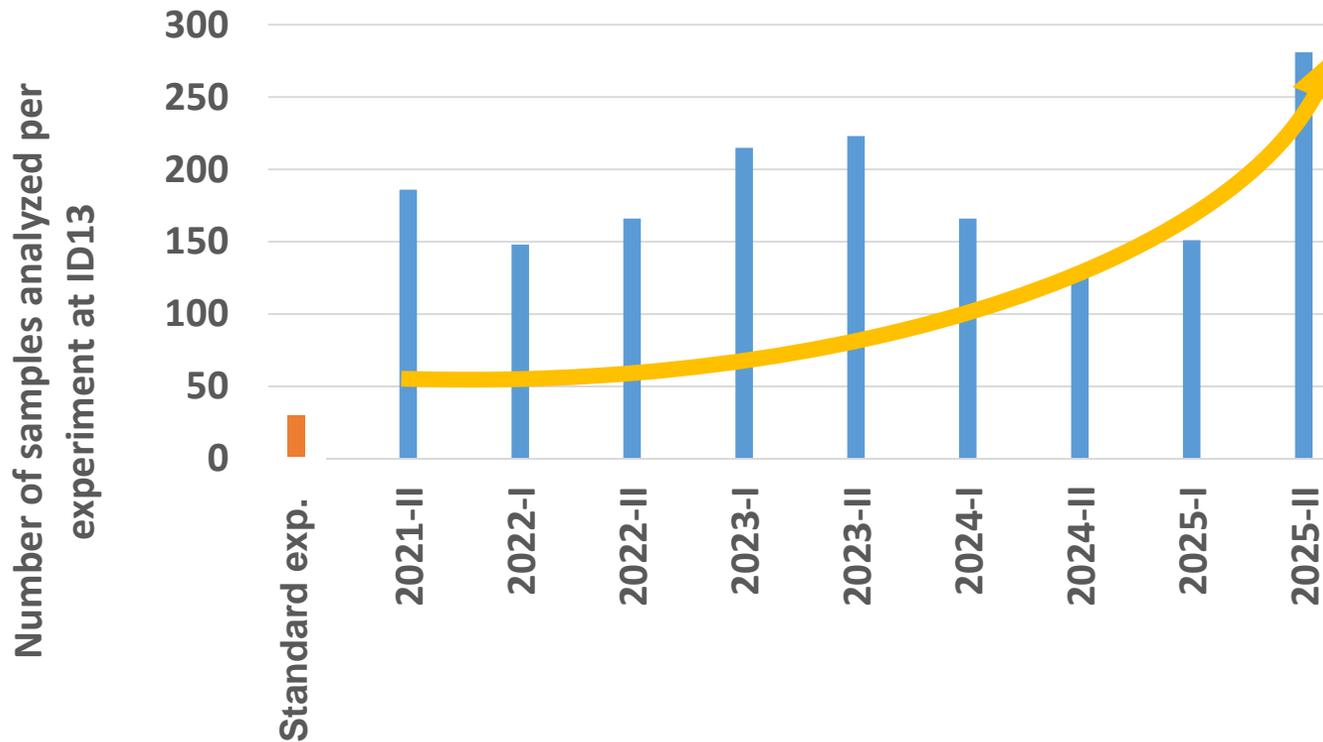
TRAINING THROUGH EXPERIMENTS, COURSES AND TUTORIALS



STEPS ALONG THE RESEARCH PATH AND IMPACT OF THE ESRF UPGRADE



Already more than 2500 artistic fragments analyzed



Thanks to the Historical Materials BAG access, **we have boosted the speed of data acquisition and the number of analyzed samples.**

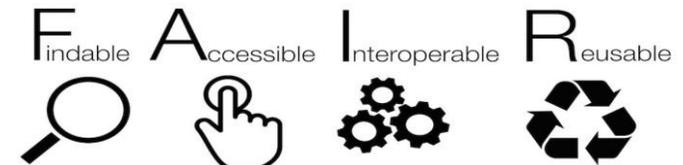
This data is as **precious** as is our heritage.

Samples:

- Various
- But belong to a unique scientific community
- ⇒ similar classes & vocabulary

2 stable set-ups:

- Stable experimental configuration
- Stable data acquisition procedure
- Stable data processing procedure
- Stable data format



THE SHARE-OSCARS PROJECT

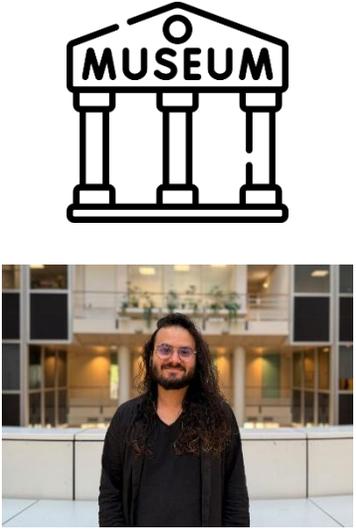


Info about the instruments and about data acquisition

Raw data

Database to search and find data and metadata

Info about the sample/object



Software + interface to (re-) analyze data

New knowledge about our heritage!





Li-Hill, 2019, Grenoble

**Thank you for your presence
and your attention!**



**Particular thanks to all colleagues involved in
beamlines development and maintenance, in the
operation of the ESRF and
to all users, ESRF colleagues and services making
this research possible**

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