Li-Hill, *The power of acceleration*, 2019,
Grenoble, rue des Montagnes Russes

The refurbished ID21 beamline at the ESRF, Nano-spectroscopy in the tender X-ray domain

Marine Cotte

On behalf of the ID21 team

The European Synchrotron | ESRF

TWO ILLUSTRATIVE CASE STUDIES: CADMIUM IN *THE SCREAM* AND IN CACAO BEANS

THE Science BREAKER
SCIENCE MEETS SOCIETY

SUBMIT YOUR ARTICLE
PROPOSE A TOPIC

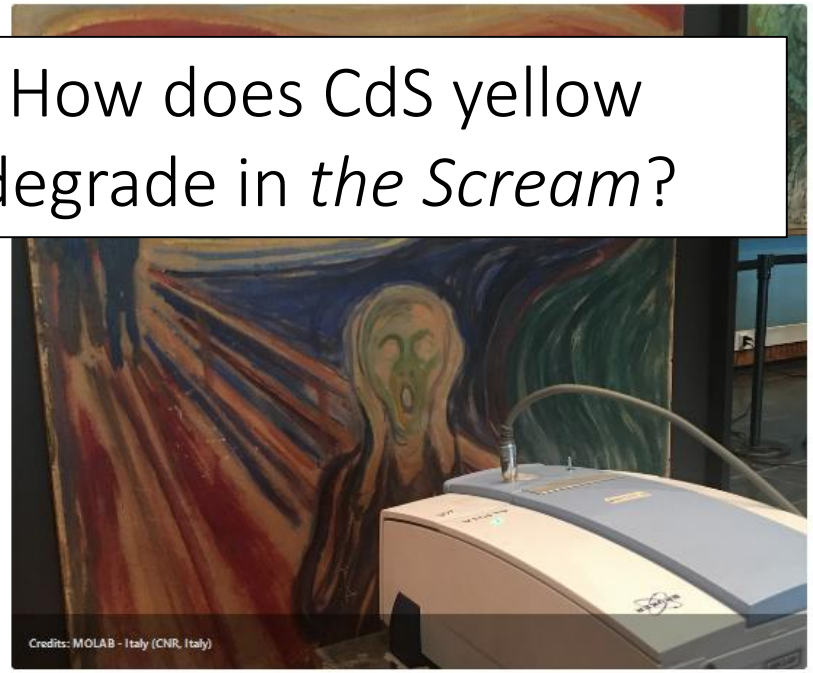
HOME | PRESENTATION | SUBJECTS | ISSUES | FOR AUTHORS | CONTACT

synchrotron radiation | spectroscopy | pigments degradation | paintings conservation | cadmium sulfide

Maths, Physics & Chemistry

Saving the cadmium yellow pigments in The Scream

In situ non-invasive spectroscopic methods combined with synchrotron radiation X-ray techniques allowed us to unveil that moisture, but not light, is the main factor triggering the degradation of cadmium yellow paints in The Scream (ca. 1910) by Edvard Munch (Munch Museum, Oslo). The findings will contribute to preserve the masterpiece, which is rarely exhibited due to its tendency to degrade.



How does CdS yellow degrade in *the Scream*?

Clima-LoCa
Fostering low-cadmium and climate-relevant innovations to enhance the resilience and inclusiveness of the growing cocoa sectors in Colombia, Ecuador and Peru

DeSIRA PARTNERSHIPS FOR INNOVATION
Funded by the European Union
Alliance Bioversity International | CIAT
CGIAR

Briefing Note No. 1

Cadmium in cacao: why it occurs, how it is regulated, and why it is a concern for producers

First Clima-LoCa briefing note on cadmium in cacao

Neil Palmer/CIAT

What is the cadmium path from the soil to the cacao beans?

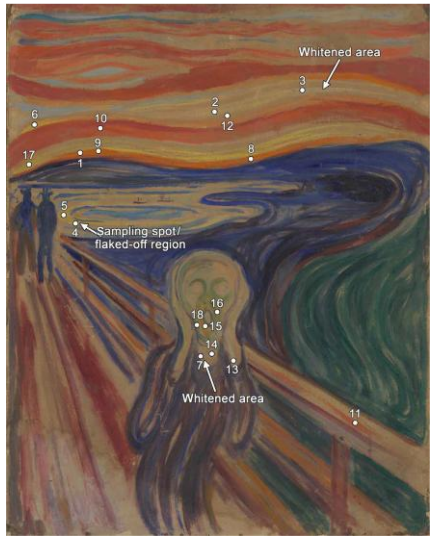
acceptable concentrations of cadmium in cacao products such as chocolate and cocoa powder.

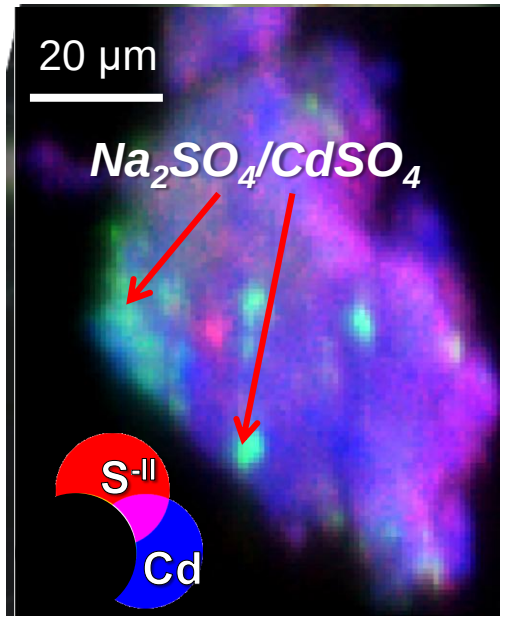
This has ramifications for the cacao sector worldwide as many farmers, particularly in Latin America and the Caribbean, may lose market access if they cannot meet these regulations.

Actors across the cacao value chain, including farmers, must be informed and supported to adapt to these regulations.

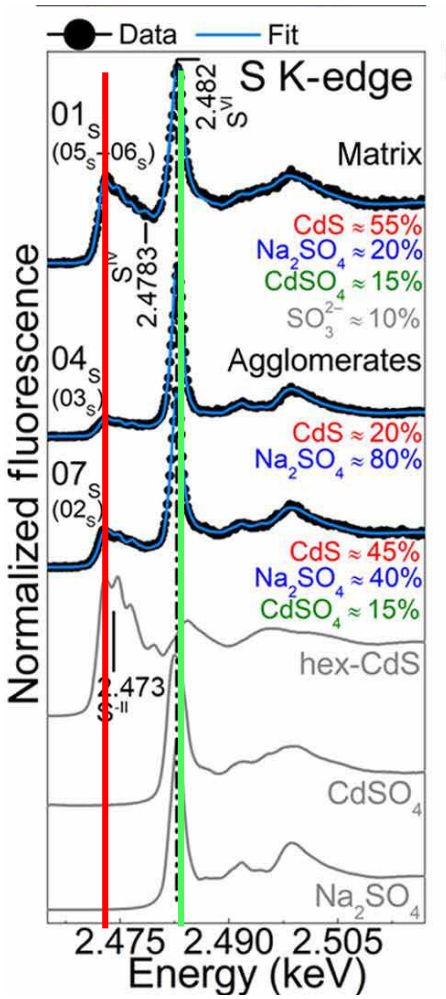
November 2021

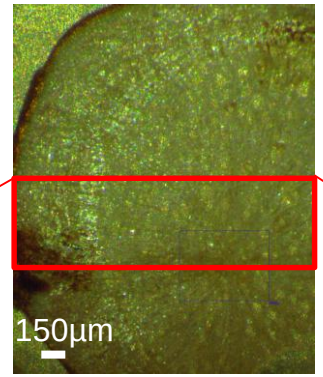
TWO ILLUSTRATIVE CASE STUDIES: CADMIUM IN THE SCREAM AND IN CACAO BEANS

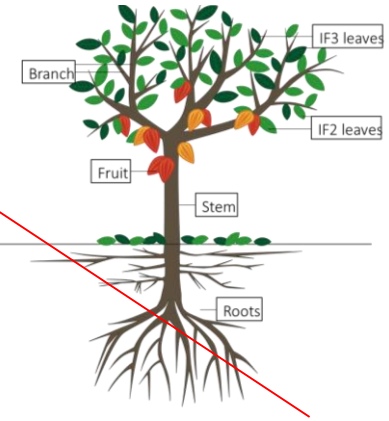


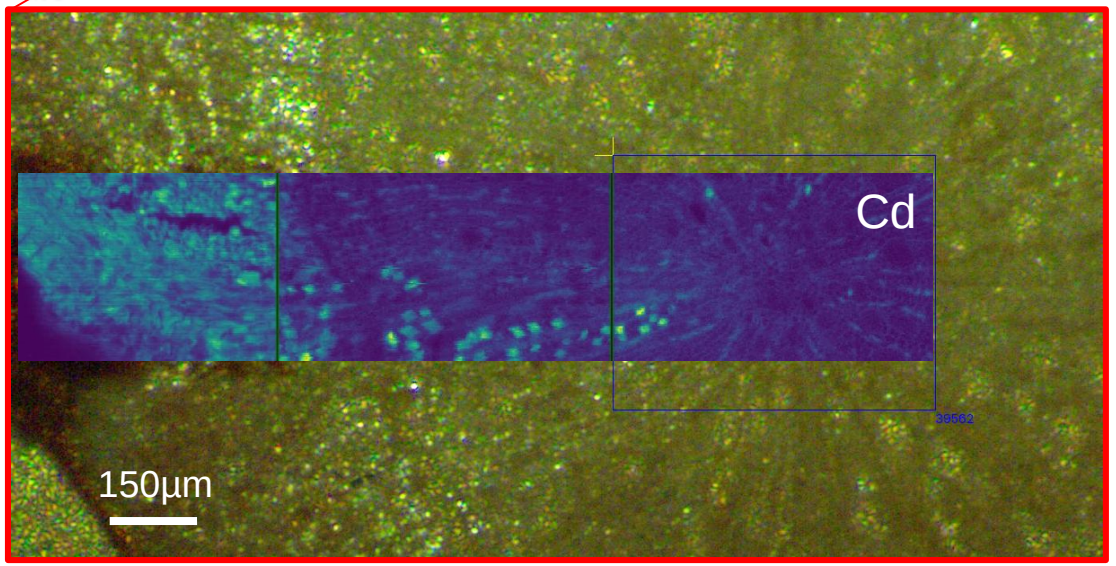


Monico, 2020







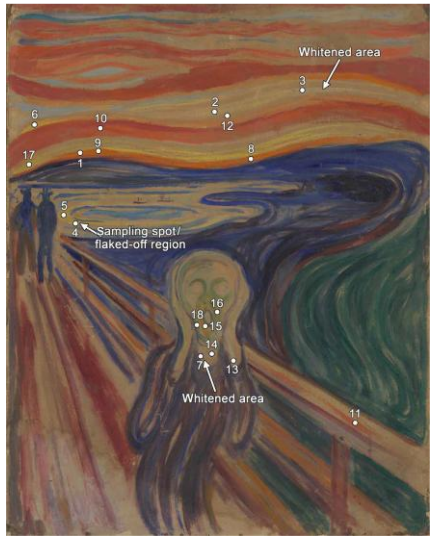


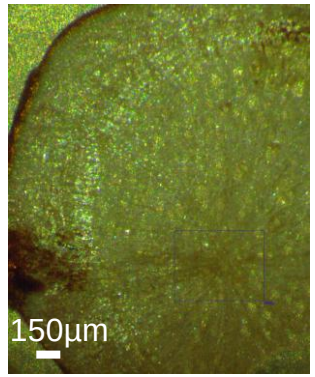
- 2D micro X-ray fluorescence maps
- Micro X-ray absorption spectra
- 2D multi-spectral mapping

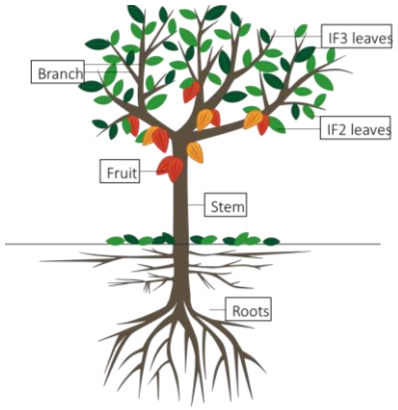
(same µXRF map acquired at n energies)

Blommaert, 2024

TWO ILLUSTRATIVE CASE STUDIES: CADMIUM IN THE SCREAM AND IN CACAO BEANS







SCIENCE ADVANCES | RESEARCH ARTICLE

CHEMISTRY

Probing the chemistry of CdS paints in *The Scream* by in situ noninvasive spectroscopies and synchrotron radiation x-ray techniques

Letizia Monico[1,2,3]*, Laura Cartechini[1,2], Francesca Rosi[1,2], Annalisa Chieli[1,2], Chiara Grazia[1,2], Steven De Meyer[3], Gert Nuyts[3], Frederik Vanmeert[3], Koen Janssens[3,4], Marine Cotte[5,6], Wout De Nolf[5], Gerald Falkenberg[7], Irina Crina Anca Sandu[8], Eva Storevik Tveit[8], Jennifer Mass[9,10], Renato Pereira de Freitas[1,11], Aldo Romani[1,2], Costanza Miliani[1,2,12]*

Contents lists available at ScienceDirect

Environmental and Experimental Botany

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

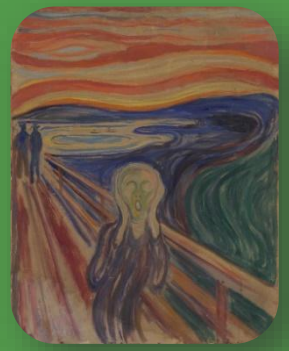
Research Paper

Ca-oxalate crystals are involved in cadmium storage in a high Cd accumulating cultivar of cacao

Hester Blommaert[a,*], Hiram Castillo-Michel[b], Giulia Veronesi[c], Rémi Tucoulou[b], Jacques Beauchêne[d], Pathmanathan Umaharan[e], Erik Smolders[f], Géraldine Sarret[a,*]

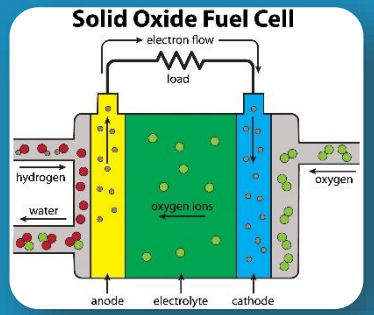
ID21: NANO X-RAY SPECTROSCOPY IN THE TENDER X-RAY DOMAIN

Cultural Heritage



- What are the masters' secrets?
- Why and how do artworks degrade?

Manufactured materials



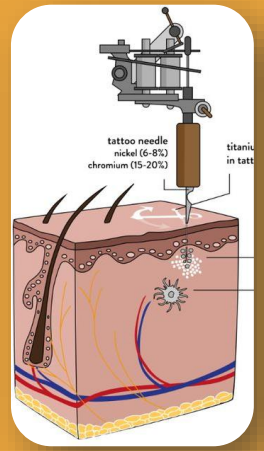
- Efficiency and stability of manufactured materials
- Chemical reactions at boundaries in electrodes, catalysts and micro-electronics

Identification and location of chemical markers in complex materials

Environmental science

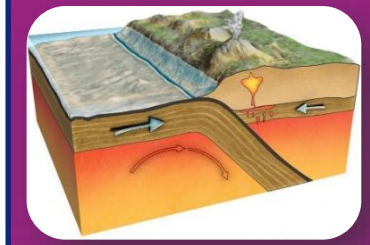
- Positive and negative impacts of materials in the environment
- Metal accumulation in plants

Health



- Interactions of manufactured materials (drugs, implants, tattoos, etc.) with living systems
- Metal homeostasis disruption in diseases

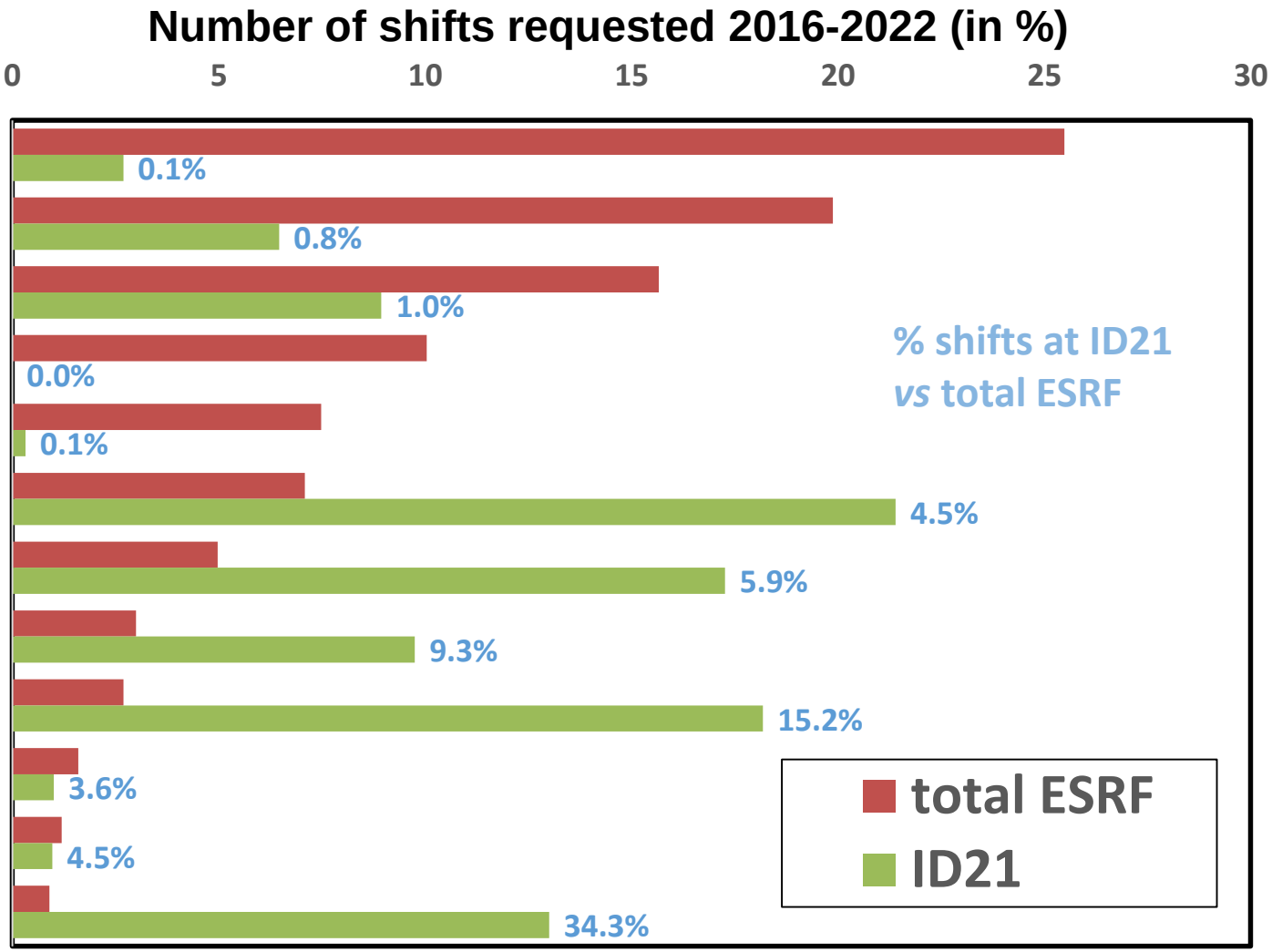
Earth and planetary sciences



- Chemical signature (element composition, trace elements, speciation) of geological processes
- Paleoclimate

ID21 WELCOMES SCIENTIFIC MINORITIES!

- **HC** Hard Condensed Matter Science
- **MA** Applied Material Science
- **CH** Chemistry
- **MX** Structural Biology
- **SC** Soft Condensed Matter Science
- **ES** Earth Science
- **LS** Life Sciences
- **MD** Medicine
- **EV** Environment
- **MI** Methods and Instrumentation
- **ME** Engineering
- **HG** Cultural Heritage



Distribution of proposals per scientific field

DIFFERENT SCIENTIFIC FIELDS BUT COMMON ANALYTICAL CHALLENGES

Graphical interfaces for navigation and data collection

Automation Workflows

- Expert users, but also often first time users who aim at

- **identifying and localizing various species** (major, minor and trace; crystallized and amorphous),

XRF and XANES

High detection limits (down to ppm)

- containing both **low Z elements and metals**

Under vacuum
Energy from 2.1 to 10keV

Cryo preservation
Expertise, instruments and assistance for sample preparation

- in **complex and heterogeneous** (often biological) matrices,

Mapping capabilities
In-line optical microscope

Focused X-ray beam

- with **sub-micrometric resolution** and **sub-millimetric 2D field of view**

Sample stage + control for fast scanning

METALS IN BIOLOGICAL SYSTEMS: TECHNICAL CHALLENGES DRIVING THE ID21 REFURBISHMENT

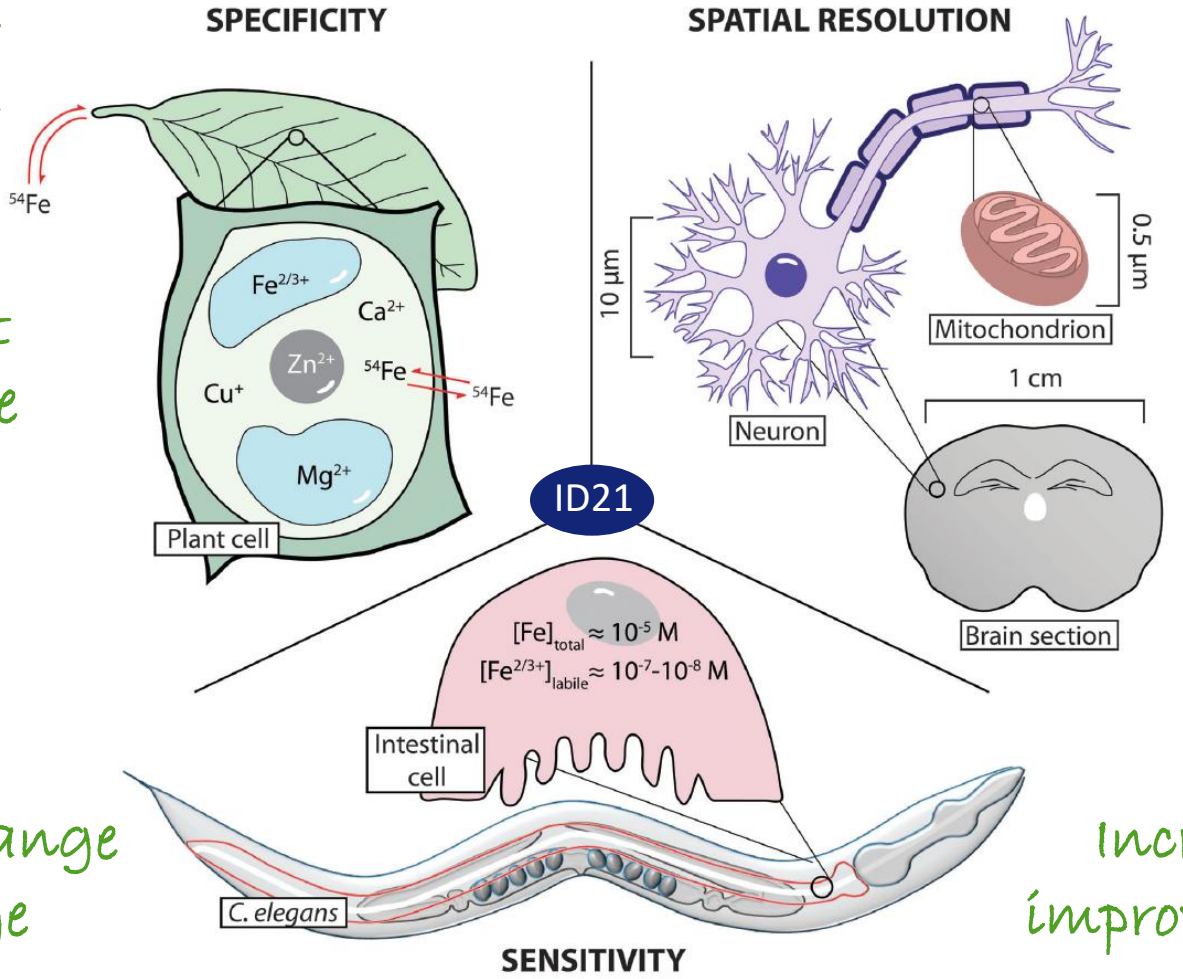
- Imaging of metals and nano-materials in biology is a balance of sensitivity, selectivity and spatial resolution.
- Disruption of the native chemical environment, during sample preparation and analysis, should be minimised.

Better combination of spectroscopy and mapping

Better management of radiation damage

Better data management

Increased energy range up to Zn K-edge



Down to 100nm But preserving the field of view and sample corpus

More stable beam during XANES scans

Increased flux and improved XRF detection

Hare et al., Chem Soc Rev, 2015

THE ID21 REFURBISHMENT

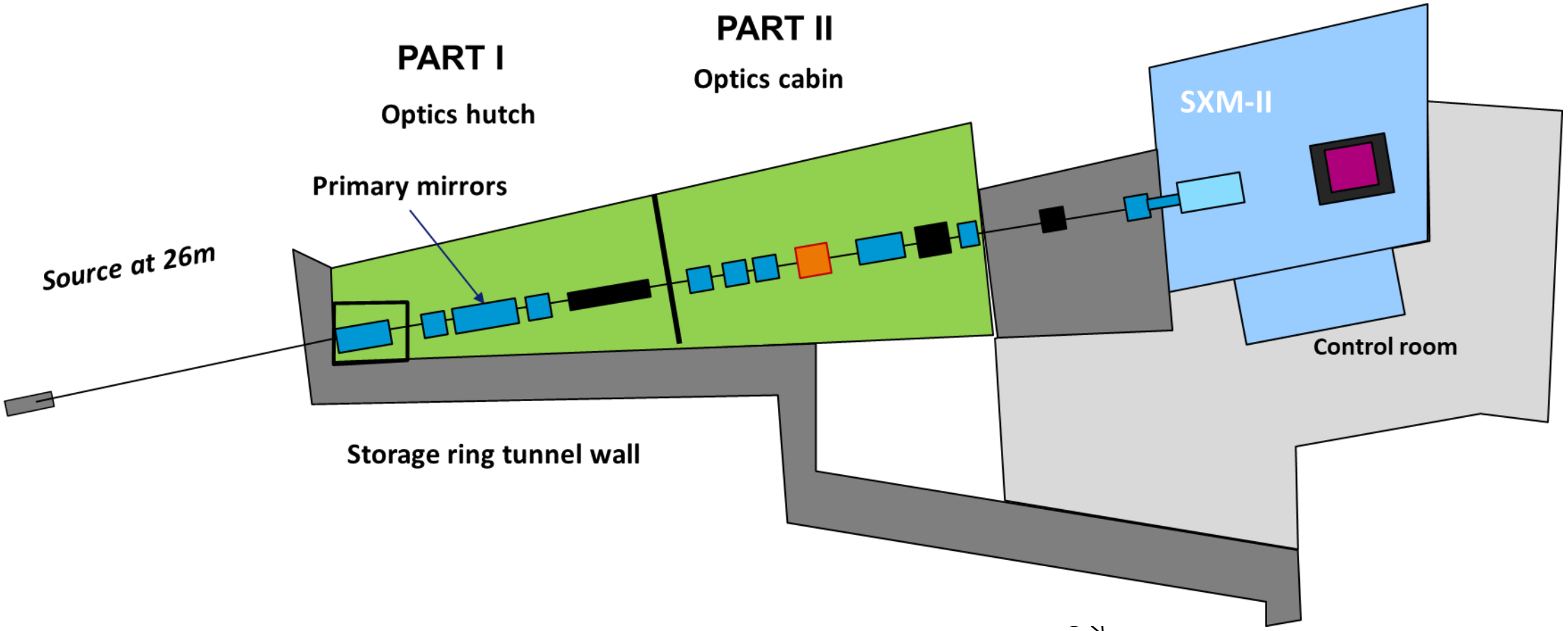
2016-2024

Part I: primary double mirrors and optics hutch, 2015-2018, coordinated by Murielle Salomé

Part II: new DCM and optics cabins, 2017-2023, coordinated by Bob Baker (for DCM) and Keith Martel (for ID21)

Part III: new nanoscope and experimental hutch, 2018-2024, coordinated by Hiram Castillo

EVOLUTION OF ID21 INSTRUMENTS, 2016-2024



09/2018: installation of the new primary mirrors

11/2018: Installation of the new DCM

29/01/20: First EBS beam

10/2020: First EBS users (remote, BLISS, Daiquiri)

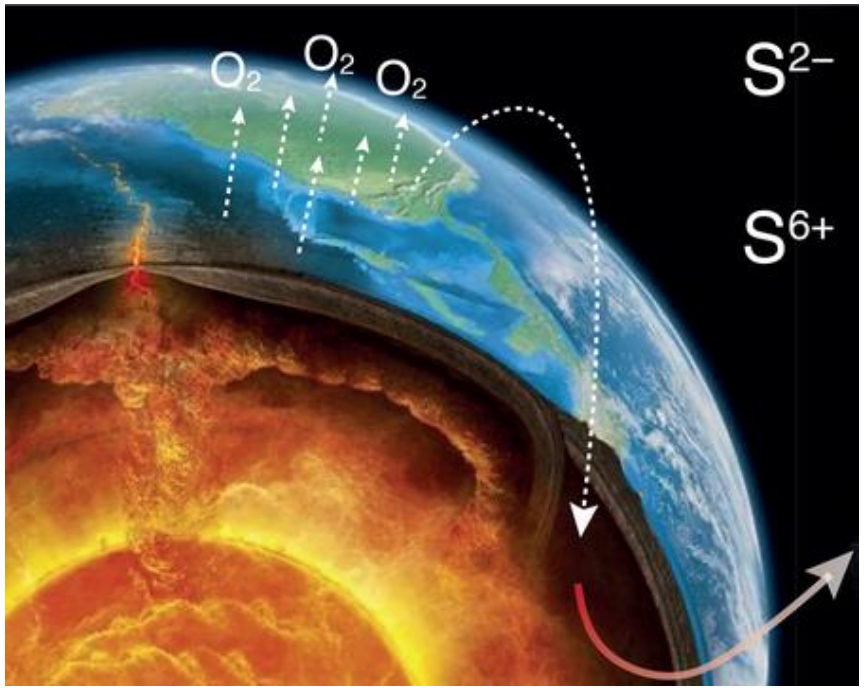
shutdowns

USM

2016 2017 2018 2019 EBS 2020 2021 2022 2023

Measuring the oxidation state of mantle-derived magmas to assess the role of plate tectonics in atmospheric oxygenation

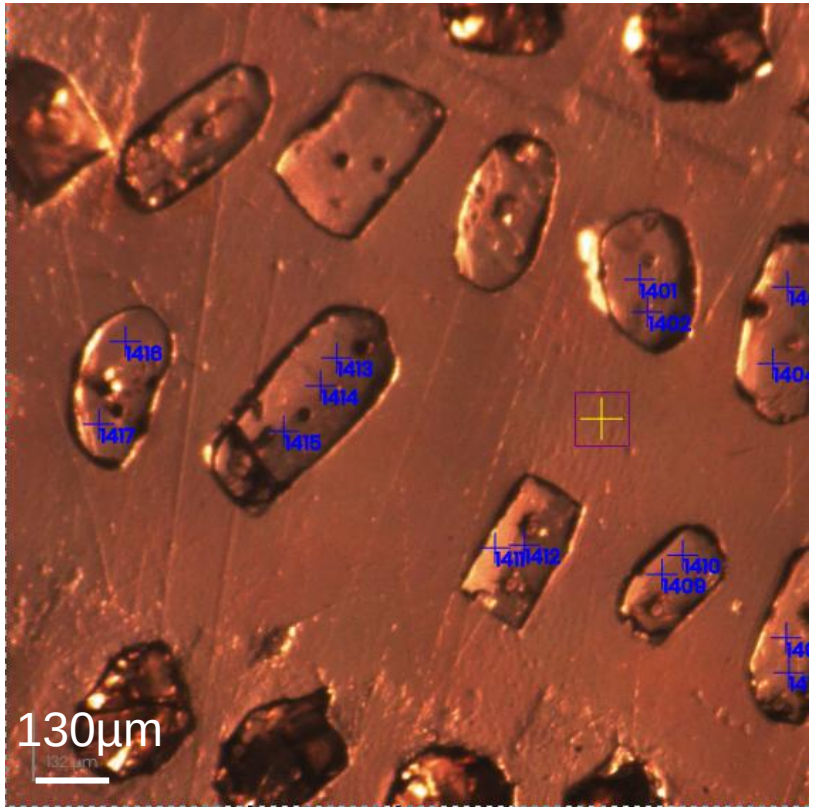
Proposal	Beamline	Start	End	Release date	Data Management Plan
ES-942	ID21	08/10/2020 08:00	13/10/2020 08:00	12/10/2023	No DMP

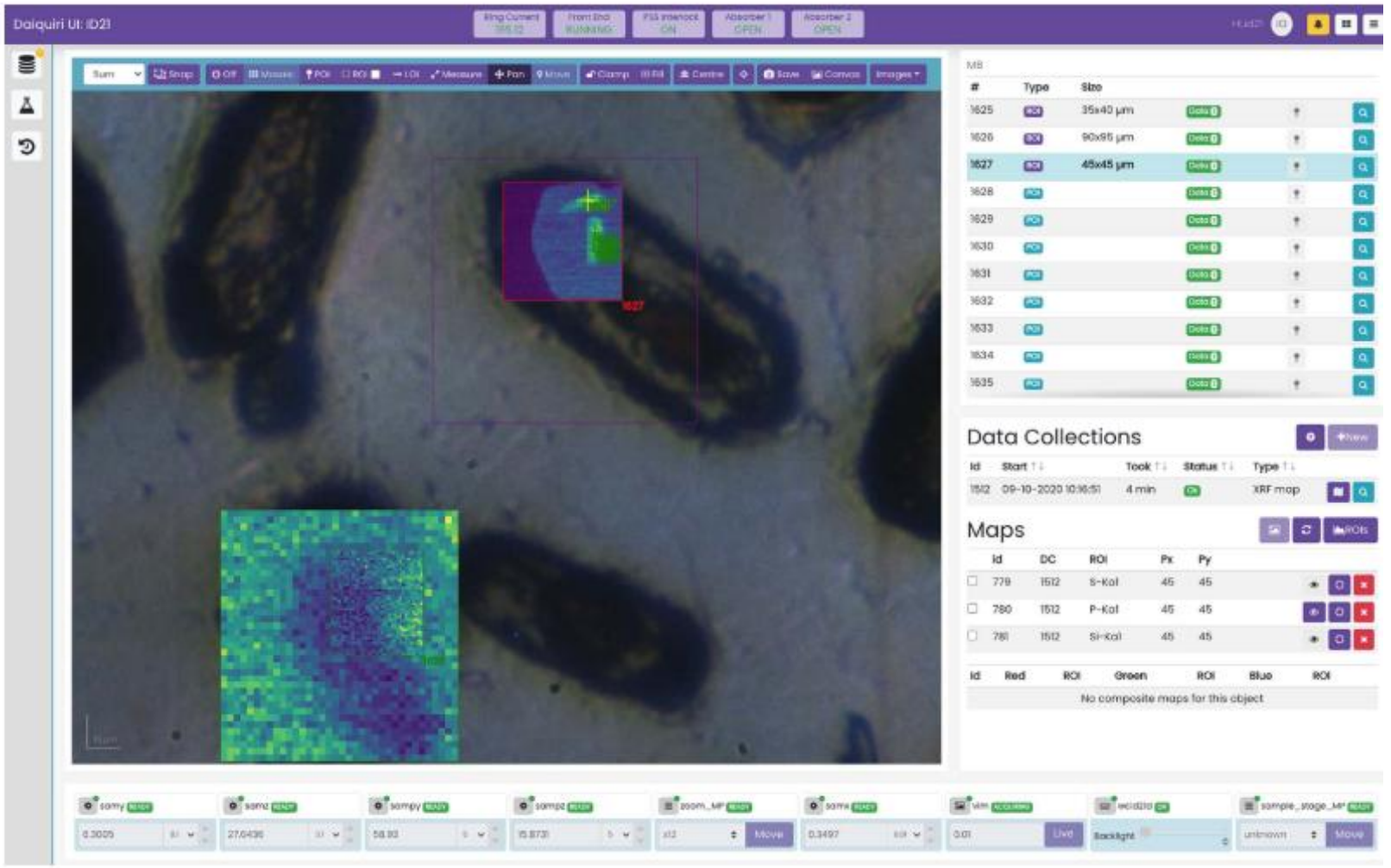


Bruno DHUIME	Participant, Proposal scientist
Craig STOREY	Participant, Proposal scientist
Emilie BRUAND	Participant, Proposal scientist
Hiram CASTILLO	Local contact
Hugo MOREIRA	Participant, Principal investigator
James DARLING	Participant, Proposal scientist
Marine COTTE	Local contact

FIRST USERS POST EBS (H. MOREIRA ET AL.), ENJOYING BLISS AND DAIQUIRI (SEPT 2020)!

Apatite inclusions hosted in 2.4–2.1-billion-year-old igneous zircons from the Mineiro Belt, Brazil.





computer programs

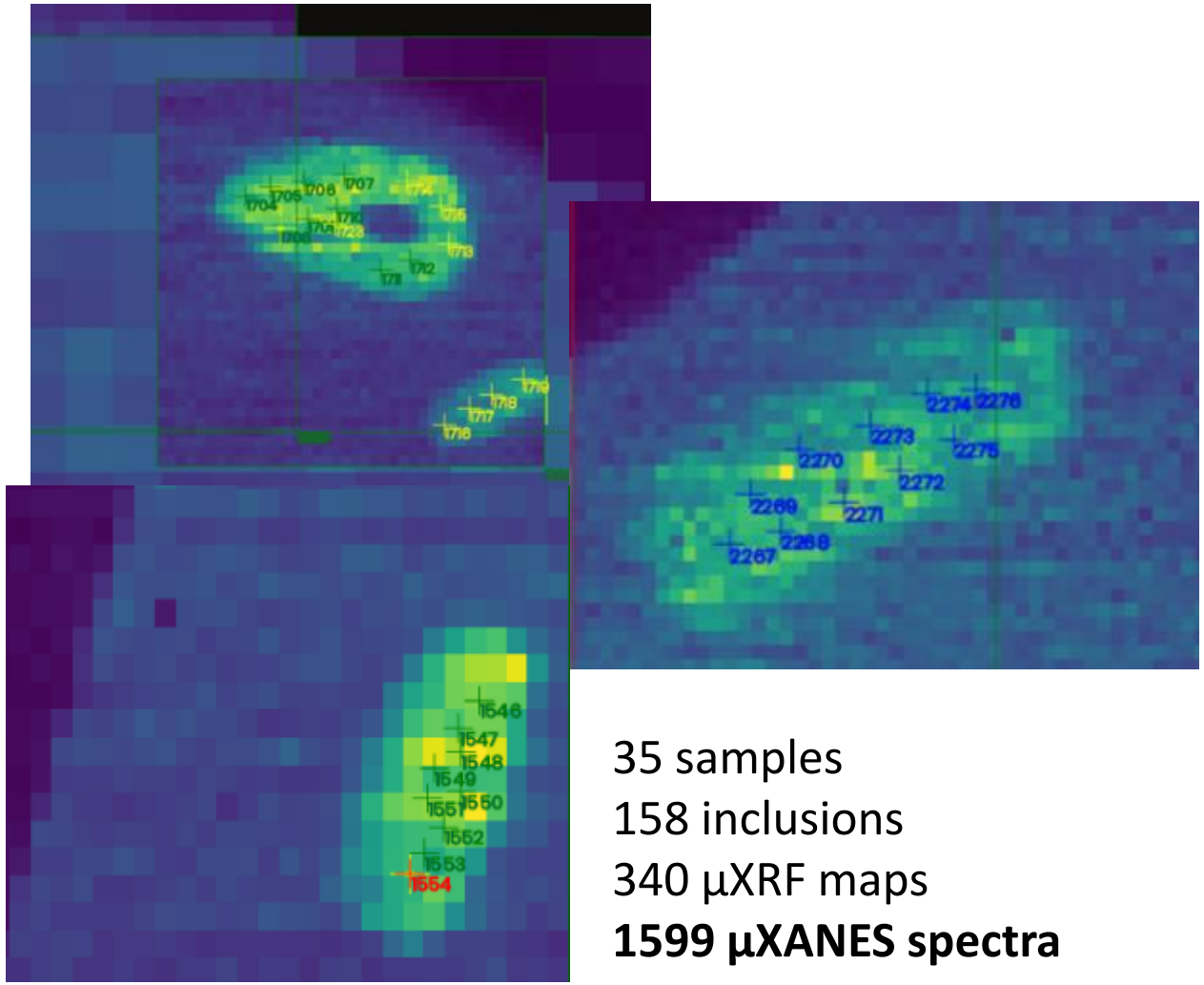
JOURNAL OF SYNCHROTRON RADIATION

ISSN 1600-5775

Daiquiri: a web-based user interface framework for beamline control and data acquisition

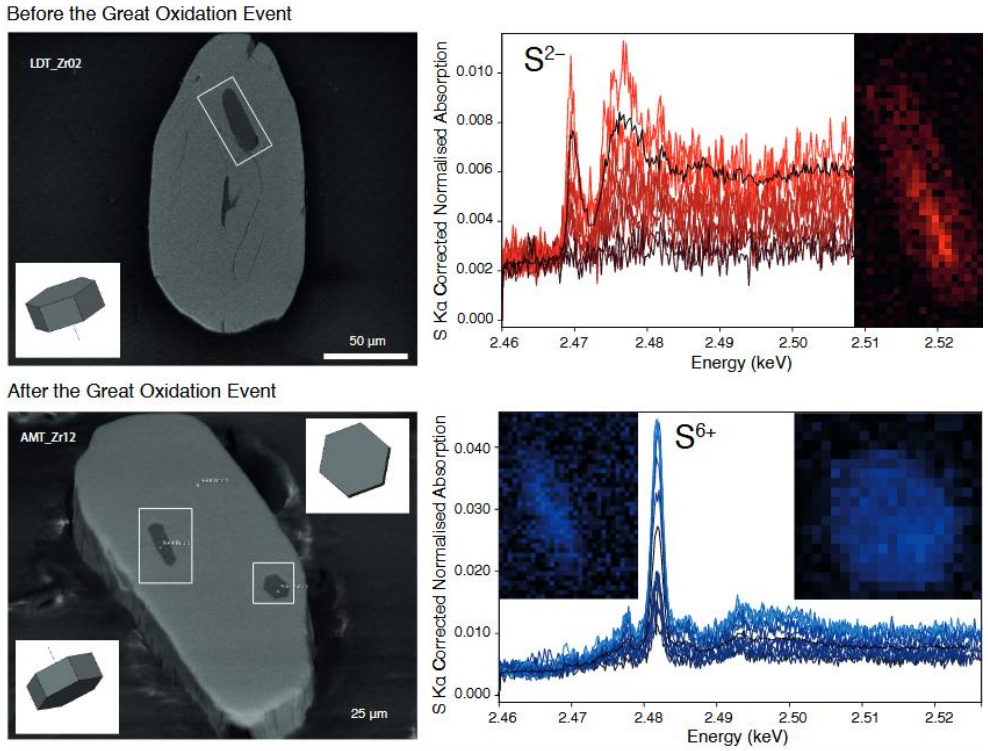
Stuart Fisher,[a]* Marcus Oscarsson,[a] Wout De Nolf,[a] Marine Cotte[a,b] and Jens Meyer[a]

FIRST USERS POST EBS (H. MOREIRA ET AL.), ENJOYING BLISS AND DAIQUIRI (SEPT 2020)!



35 samples
158 inclusions
340 µXRF maps
1599 µXANES spectra

In remote and in 5 days



nature geoscience

Article

https://doi.org/10.1038/s41561-023-01258-4

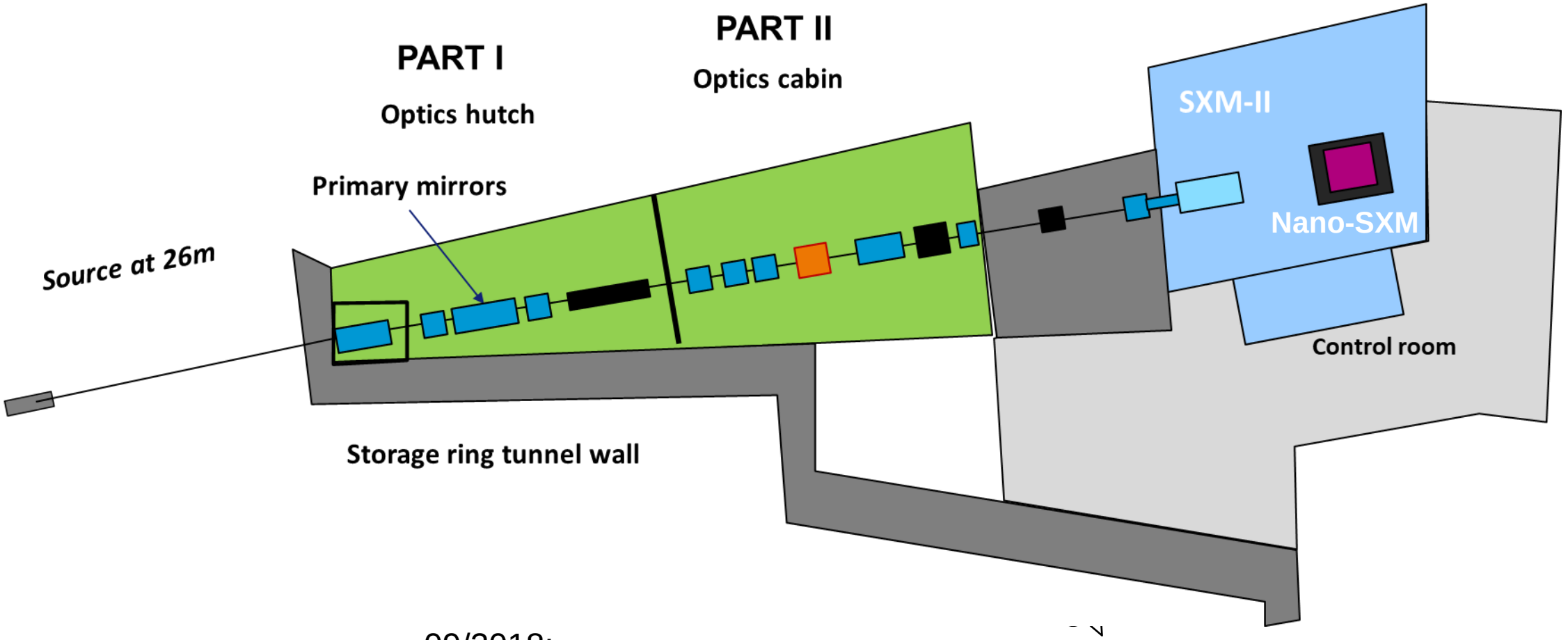
Sub-arc mantle fugacity shifted by sediment recycling across the Great Oxidation Event

Received: 27 January 2023

Accepted: 26 July 2023

Hugo Moreira[1,2,8], Craig Storey[2], Emilie Bruand[3], James Darling[2], Mike Fowler[2], Marine Cotte[4,5], Edgar E. Villalobos-Portillo[4], Fleurice Parat[1], Luís Seixas[6], Pascal Philippot[1,7] & Bruno Dhuime[1]

EVOLUTION OF ID21 INSTRUMENTS, 2016-2024



shutdowns

USM

09/2018: installation of the new primary mirrors

11/2018: Installation of the new DCM

29/01/20: First EBS beam

08/09/20: First EBS users (remote, BLISS, Daiquiri)

11/01/2023: installation nano-SXM

2016 2017 2018 2019 EBS 2020 2021 2022 2023

THE REFURBISHMENT PART III: IMPLEMENTATION OF A NEW NANOSCOPE

Main contributors:

ID21- Hiram Castillo, Murielle Salome, Gaetan Goulet, Marine Cotte, David Bugnazet,

EXPD- Jean Susini, Harald Reichert, M. Krisch, G. Martinez-Criado,

Sample environment- Yves Watier, Romain Garlet;

ISDD- François Villar, Bertrand Pelissier, Delphine Baboulin, Daniel Fiole, Olivier Hignette, Philipp Brumund, Robert Baker, Noel Levet, Philippe Tardieu, Giovani Malandrino, Eve Di Vita, Raymond Barret, Juan Reyes-Herrera, Manuel Sanchez del Rio, Cedric Cohen, Ricardo Hino, Cyril Guilloud, Stuart Fisher;

TID- Pascal Renaud, Jean-Olivier Chamond, Julien Chalaye, Stephan Arnaud, Aurelien Henriette, Laurent Besset, Yohan Guigal, Christoph Lefevre, Bruno Perret, Cristina Gonzalez, Emmanuel Alcouffe;

ADMIN- Jean-Michel Georgoux;

DIR- Stephanie Ricot, Patrick Colomp, Julien Grasseler, Paul Berkvens.

And many other ESRF colleagues that provided their expertise during our refurbishment campaign.

THE X-RAY NANOSCOPE IS NOW OPEN TO USERS!

Murielle Salomé, engineer and Hiram Castillo-Michel, ID21 scientist, at work on the beamline.

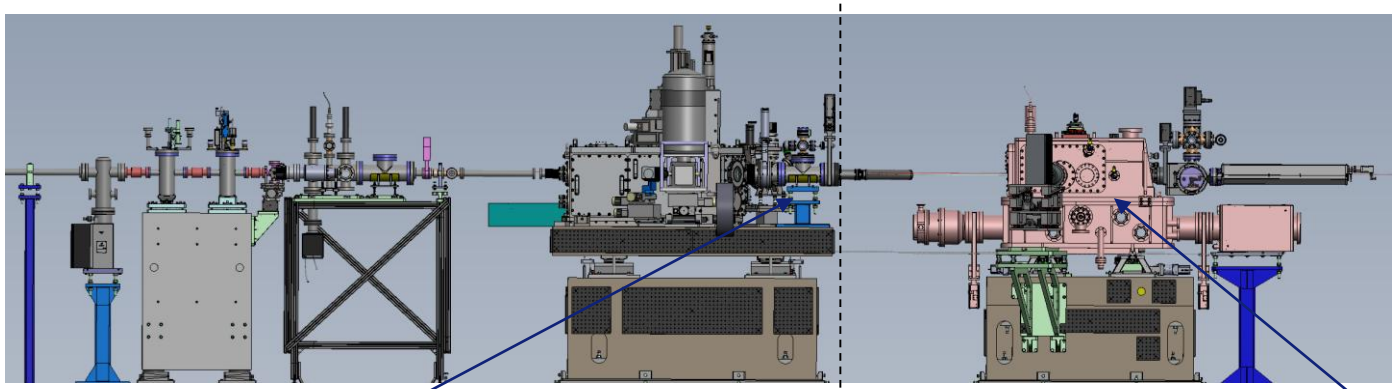
Nanoscope opens to users

Users have taken data on the ID21 nanoscope for the first time, revealing a potential to trace nanoparticles with unprecedented speed and precision. Visiting from the University of Bordeaux in France, the users have been familiarising themselves with

"The spatial resolution of the new ID21 has been paramount for the success of our experiment"

THE REFURBISHMENT PART III: IMPLEMENTATION OF A NEW NANOSCOPE (PC: H. CASTILLO-MICHEL)

X-rays



Scanning X-ray microscope (“old”)

Scanning X-ray nanoscope (new)

2-10.5keV
Micro/ Nano X-ray fluorescence
Micro/ Nano X-ray Absorption Spectroscopy
Multi-energy maps
Under vacuum; Cryo / Room temperature

- Unfocussed beam (100-300µm)
  or focussed beam (0.3(V)×0.7(H)µm²)
- Ni coated KB => no access to Ni XANES
- 1 single element XRF detector

- Only focussed beam: expected beam size down to 0.1(V)×0.1(H)µm² (**now 150×150nm² above 6keV**)
- 2 KBs (one Ni, one Pt coating) giving high flux up to 10keV
- Two 5-element XRF detectors (to be delivered soon)

Mechanical Design: F. Villar, D. Baboulin, B. Pelissier

ID21 ENERGY RANGE: 2.1-10.5KEV

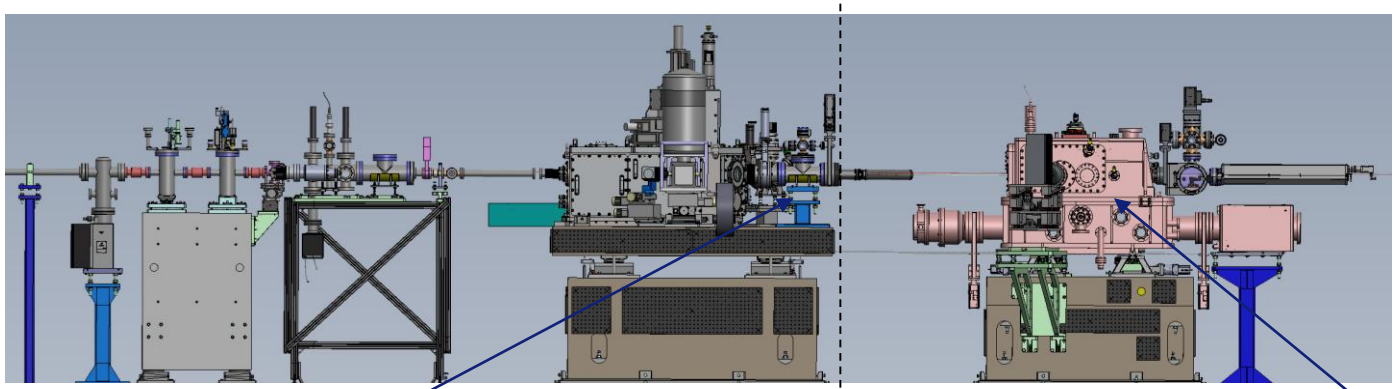
Identification of elements by X-ray fluorescence (coloured)
Identification of species by X-ray absorption spectroscopy (underlined)

K-lines **L-lines** **M-lines**

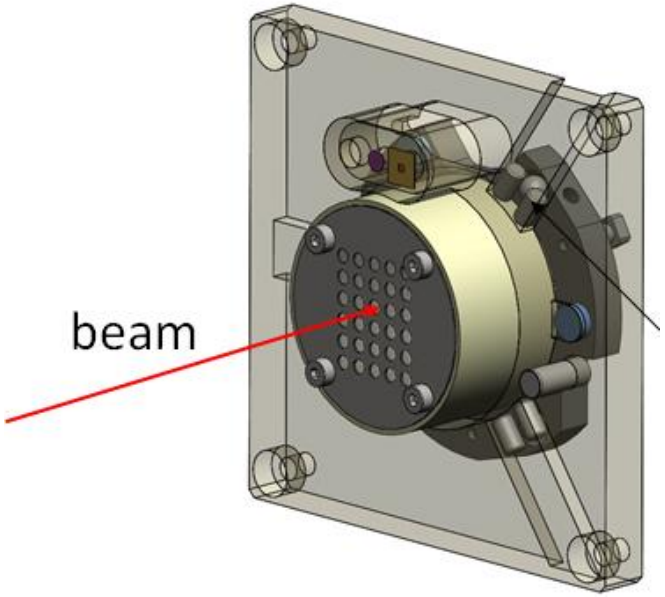
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		Uuo
Lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

THE OLD MICROSCOPE AND THE NEW NANSCOPE

X-rays

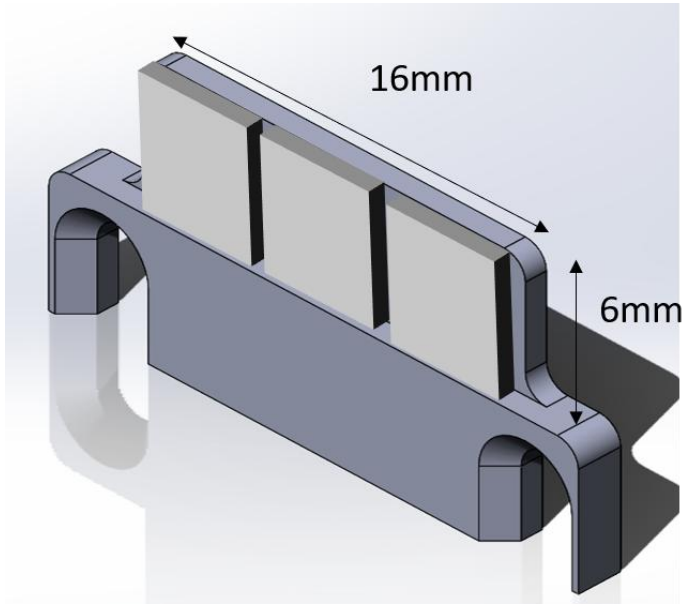


Scanning X-ray microscope (“old”)



Samples: max 25mm diameter

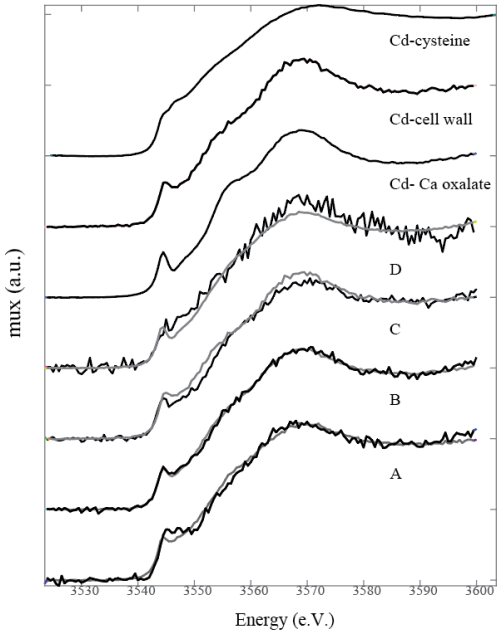
Scanning X-ray nanoscope (new)

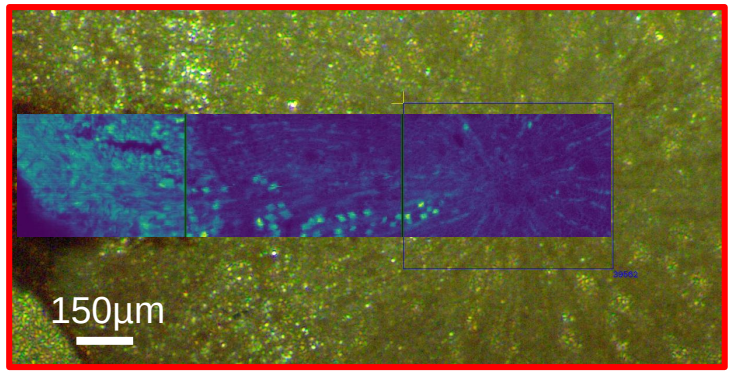


Samples: max 16mm hor, 6mm ver

NANO-XANES ON BIOLOGICAL SAMPLES IMPROVED THANKS TO EBS AND TO THE REFURBISHMENT

Tracking trace elements

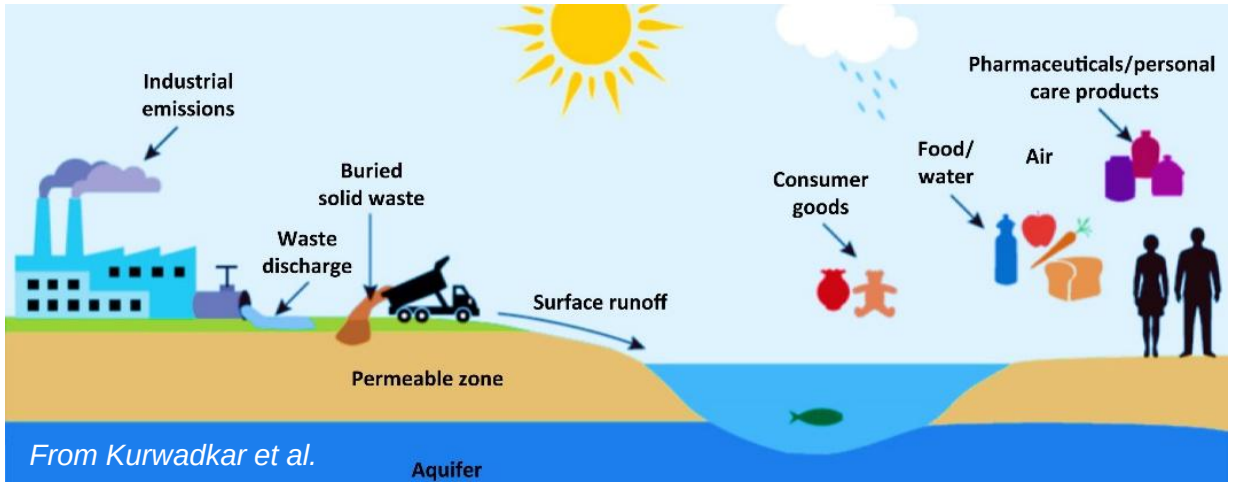




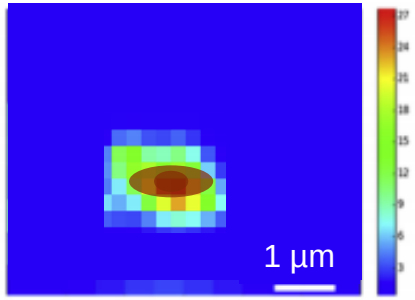
Cd concentration in the **ppm level**.

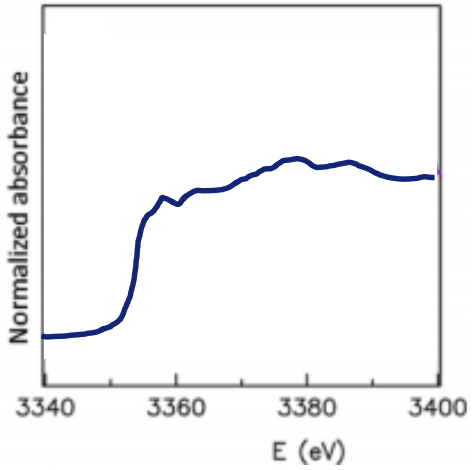
µXRF maps and µXANES only feasible thanks to **EBS flux**.

XANES on nanoparticles



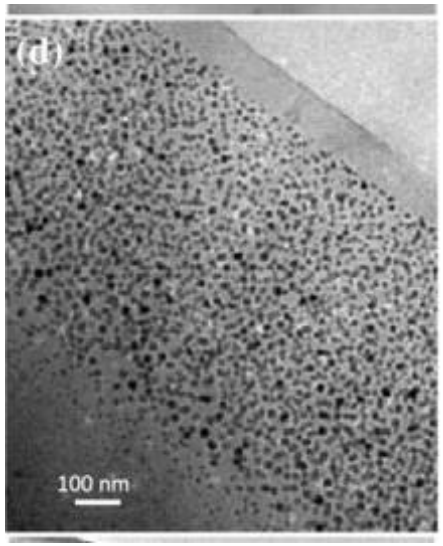
With the new chromatic aberration corrector and the new nanoscope





Copper speciation in lustre layers

Proposal	Beamline	Start	End	Release date	DOI
MA-6420	ID21	25/09/2024 08:00	30/09/2024 08:00	30/09/2027	DOI 10.15151/ESRF-ES-1842758367



T. Pradell, *Nanoscience and Cultural Heritage*, 2016

Clément HOLE	Local contact
Eloi PINEDA	Participant, Scientist
Jan Berend BAAS	Participant, Scientist
Judit MOLERA	Participant, Proposal scientist
Marine COTTE	Local contact
Ruth SADURNI	Participant, Proposal scientist
Trinitat PRADELL	Participant, Principal investigator

TAKE HOME MESSAGE

ID21:

- Techniques: 2D XRF mapping, XAS (mainly XANES), hyperspectral mapping
- Under vacuum: very good detection of low Z elements
- Cryo-preservation available
- Beam size:
  - microscope from 0.3x0.7µm² to 0.3x0.3mm²,
  - nanoscope down to <150nm²
- Energy range 2-11keV (K-edge from P to Zn; access to Ag, Cd, Sb… through L-lines)

Thank you for attending the webinar!

Thanks to all users and colleagues
involved in this research,
in the maintenance and
development of our instruments!
Thanks to the ID21 team

Join us for great experiments at ID21!

cotte@esrf.fr