# Advances on MARS:
# the beamline dedicated to
# radioactive materials at Synchrotron Soleil

P.L. Solari, S. Schlutig, S. Cammelli, R. Bès, H. Hermange and S. Conradson

* ***M**ulti **A**nalyses on **R**adioactive **S**amples*

# Outline

- Overview
- Sample environment
- Experiments
- Summary

# Overview

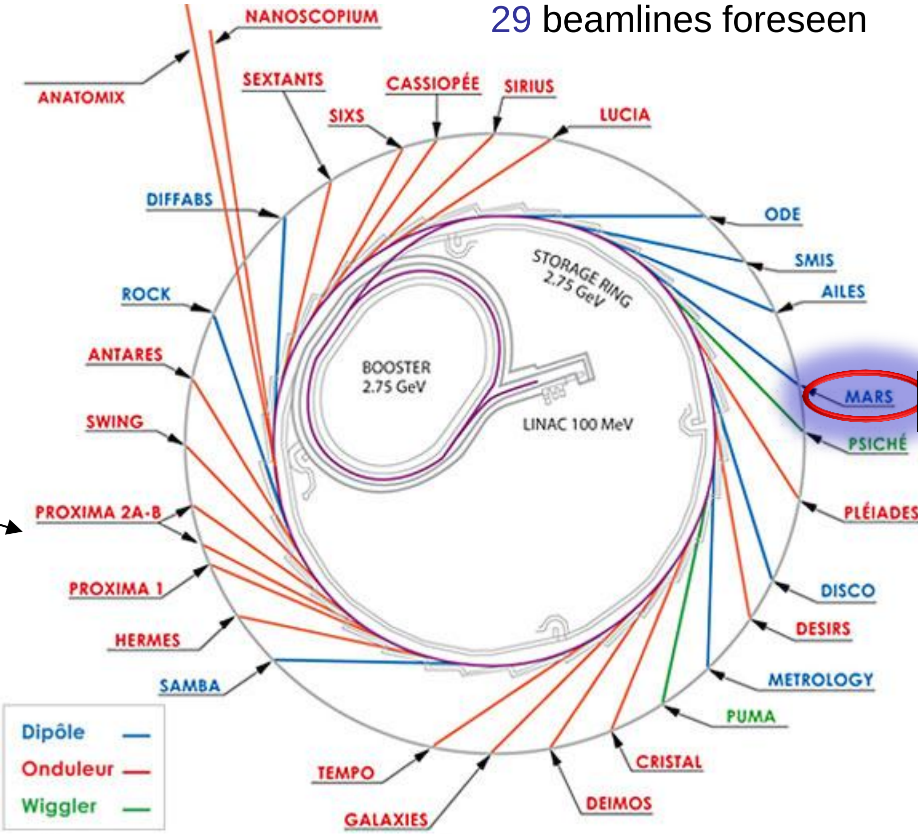
*Sitaud et al. , Journal of Nuclear Materials (2012)*

*Llorens et al. , Radiochimica Acta (2014) to be published*

# Synchrotron Soleil and MARS beamline

25 beamlines opened to users in 2014

29 beamlines foreseen




The storage ring parameters

| | |
|---|---|
| Nominal Energy | 2.75 GeV |
| Circumference | 354 m |
| Current Intensity | 430 mA (500 mA in 2015) |

Radioactive samples:
Currently only allowed on MARS beamline
(also below exemption limit)

*direct financial participation of CEA/DEN and CEA/DAM (~+30%)*

# General context and scientific needs

**The main scientific fields** associated to the MARS beamline are related to :

- studies concerning all the steps of the **nuclear fuel cycle**
- studies concerning the radionuclides impact in the **environment** and the **biological effects** of the radionuclides
- general studies on **physical and chemical properties** of radionuclides

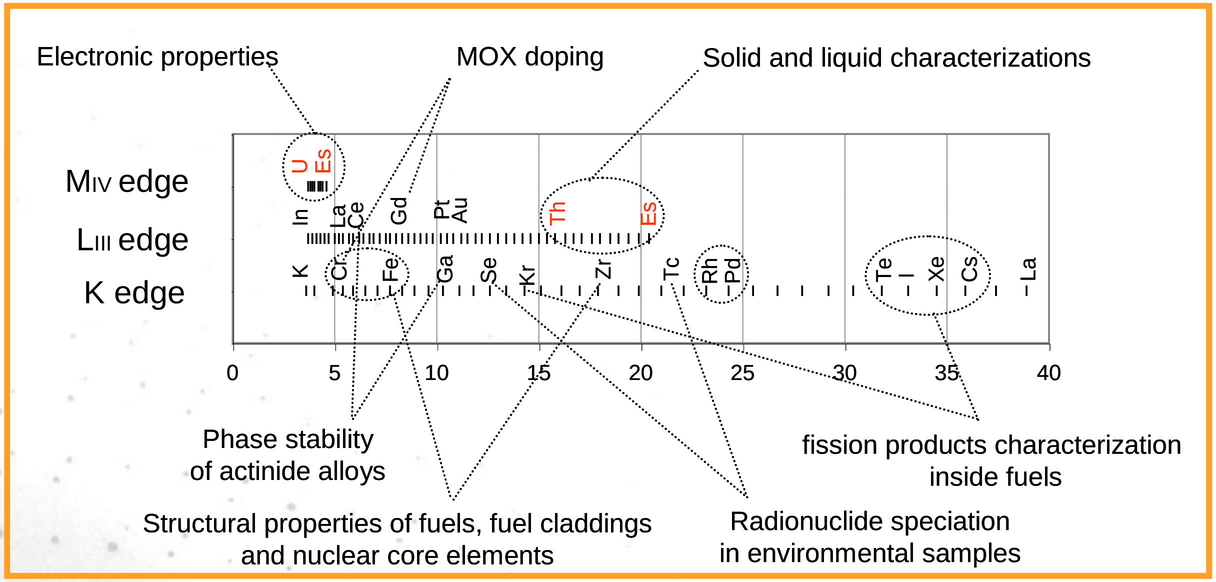
**The consequences** are that the MARS beamline must be

1) Able to accept **low to relatively high radioactive samples (from Bq to GBq)**

2) A **multi-disciplinary** beamline : Material sciences, Chemistry, Biology

3) A **multi-technique** beamline : Absorption, Fluorescence, Diffraction

**Selected X-ray energy range: from 3.5 to 35 keV**

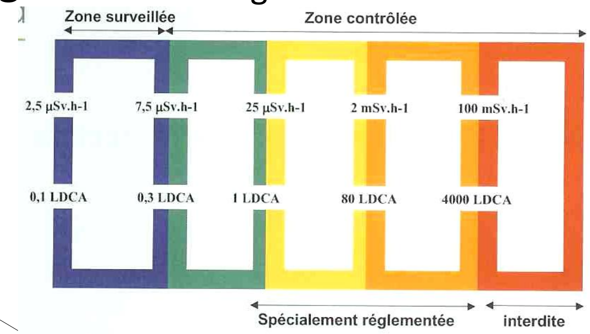


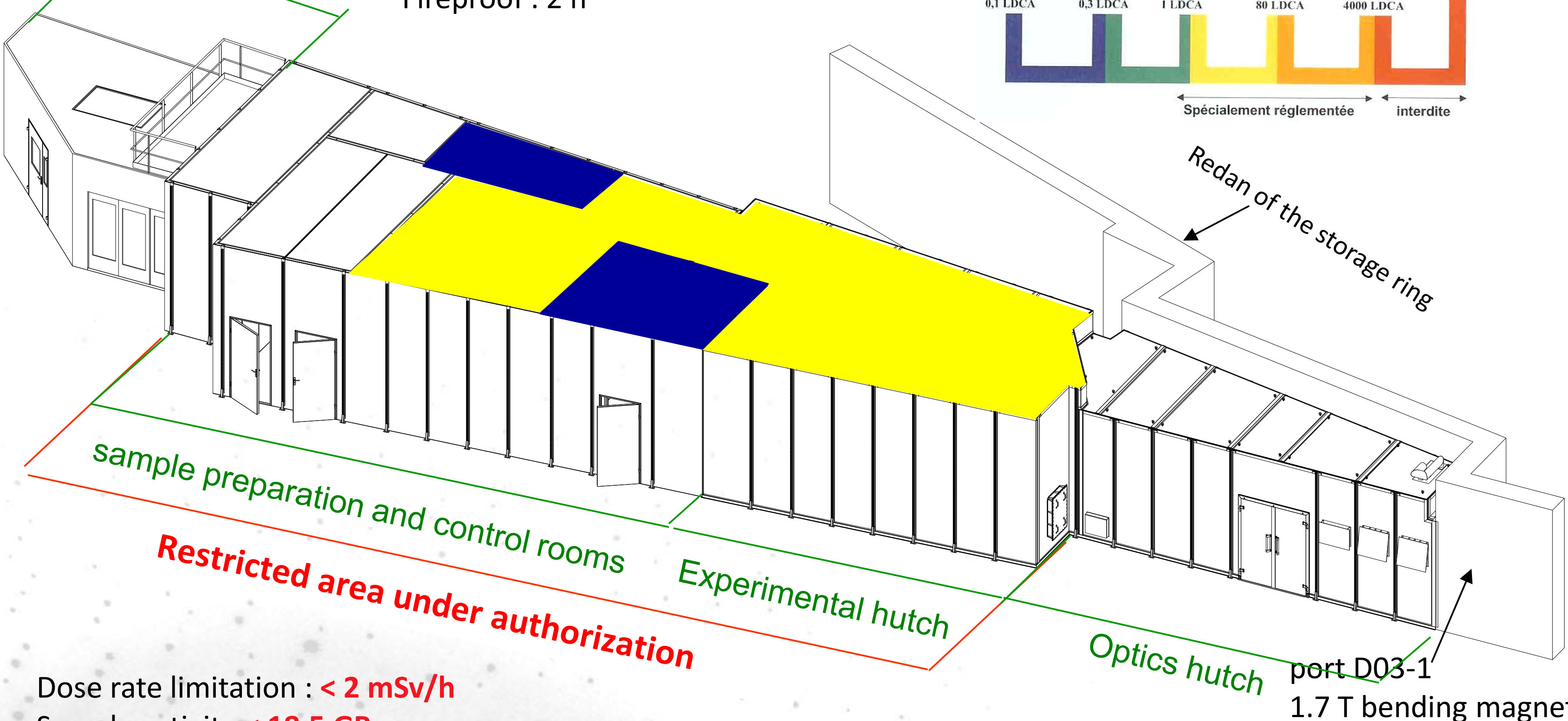
# Layout of the Mars beamline (side view)

A “hot” beamline inside a standard synchrotron building

global length : 40 m
Restricted area : ~ 100 m$^2$
Low pressure : - 80 Pa,
Fireproof : 2 h

Radiological limitations

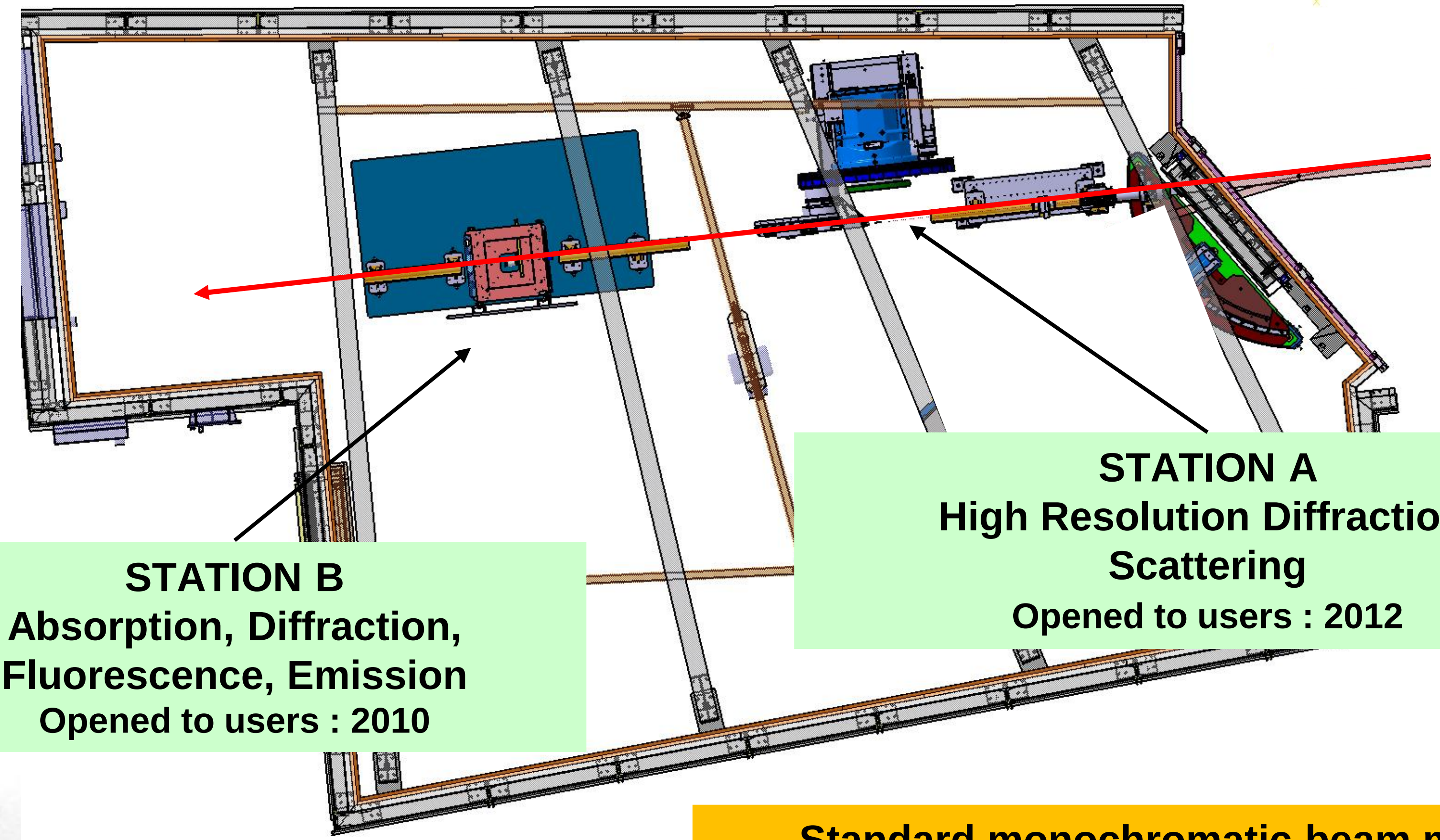



Dose rate limitation : **< 2 mSv/h**
Sample activity **< 18.5 GBq**

# Experimental hutch (top view)

## Two experimental end-stations



**STATION A**
**High Resolution Diffraction, Scattering**
**Opened to users : 2012**

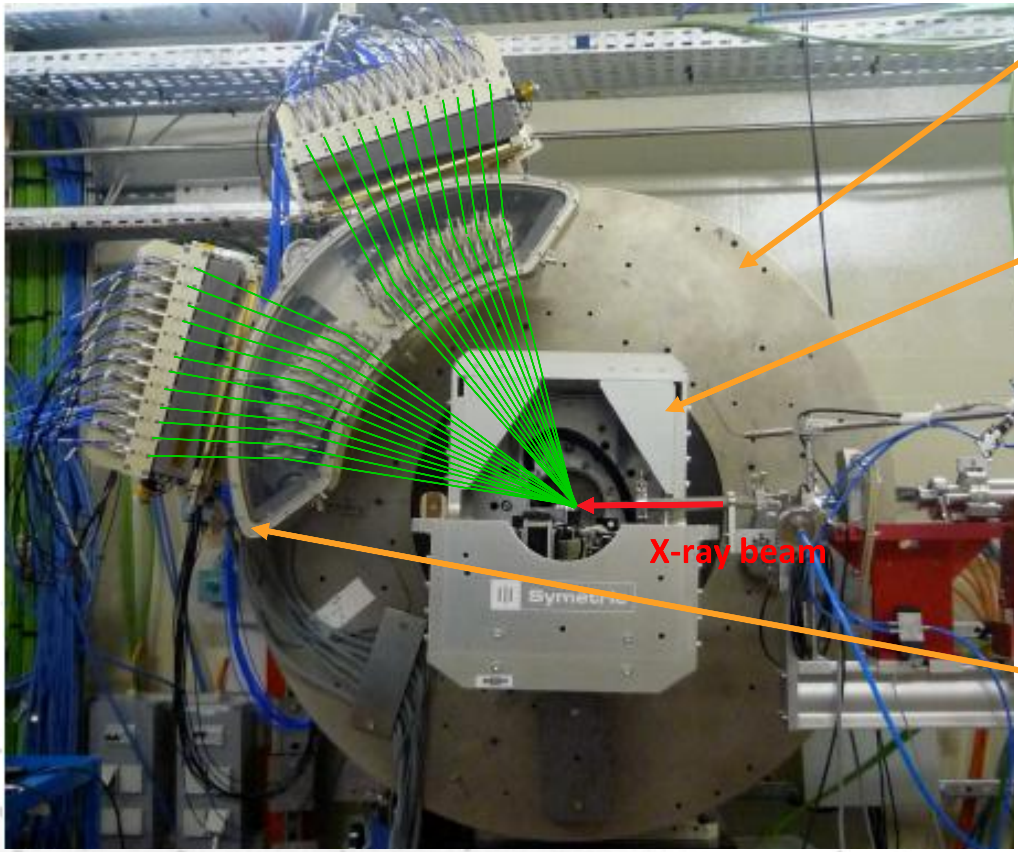
**STATION B**
**Absorption, Diffraction, Fluorescence, Emission**
**Opened to users : 2010**

**Standard monochromatic beam mode:**
**Standard spot size (HxV) ~ 400 x 300 μm$^2$**
**Flux 1x10$^{12}$ ph/s at 10 keV**

# Station A: HR diffraction and Wide Angle Scattering

XRD to WAXS measurements on polycrystalline samples (powders) or single crystals
Current energy range : from 7 to 25 keV (without focusing)

*CEA development*



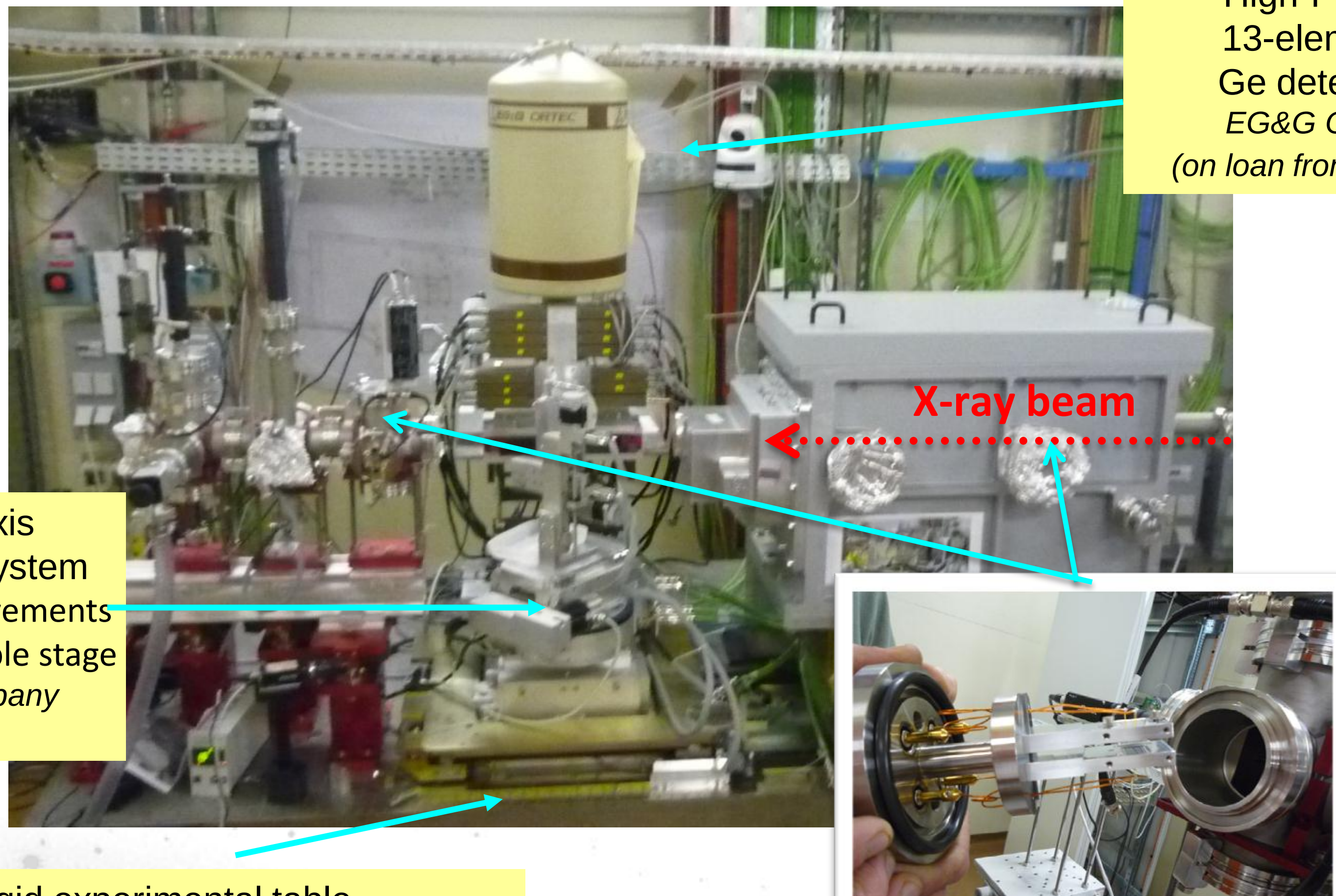

(1) **a robust diffractometer** (SMP)
→ 2 coaxial, high precision stages (θ or Ω, 2θ)

(2) **a goniometer** (CEA, Symétrie)
→ high precision χ rotation (-5 to 90°)
→ high precision φ rotation (0 to 360° )

(3) **a detection system** (CEA, COMAT)
→ multi-crystal analyzer stage concept [Hodeau 1998]
→ decrease the background radiation coming from high radioactive samples
→ 2 symmetric rows of 12 Ge(111) crystals and 12 NaI(Tl) scintillation crystals coupled on fast PM tubes giving a 24 channels (67.4°)

Typical angular resolution = 0.01° and exposure time = 1h for a full pattern

# Station B: X-ray Absorption Spectroscopy set-up




High-Purity
13-element
Ge detector
*EG&G Ortec*
*(on loan from LANL)*

Motorized six-axis
positioning stage system
with micrometric movements
and special multi-sample stage
*A-Z Systèmes Company*
*(France)*

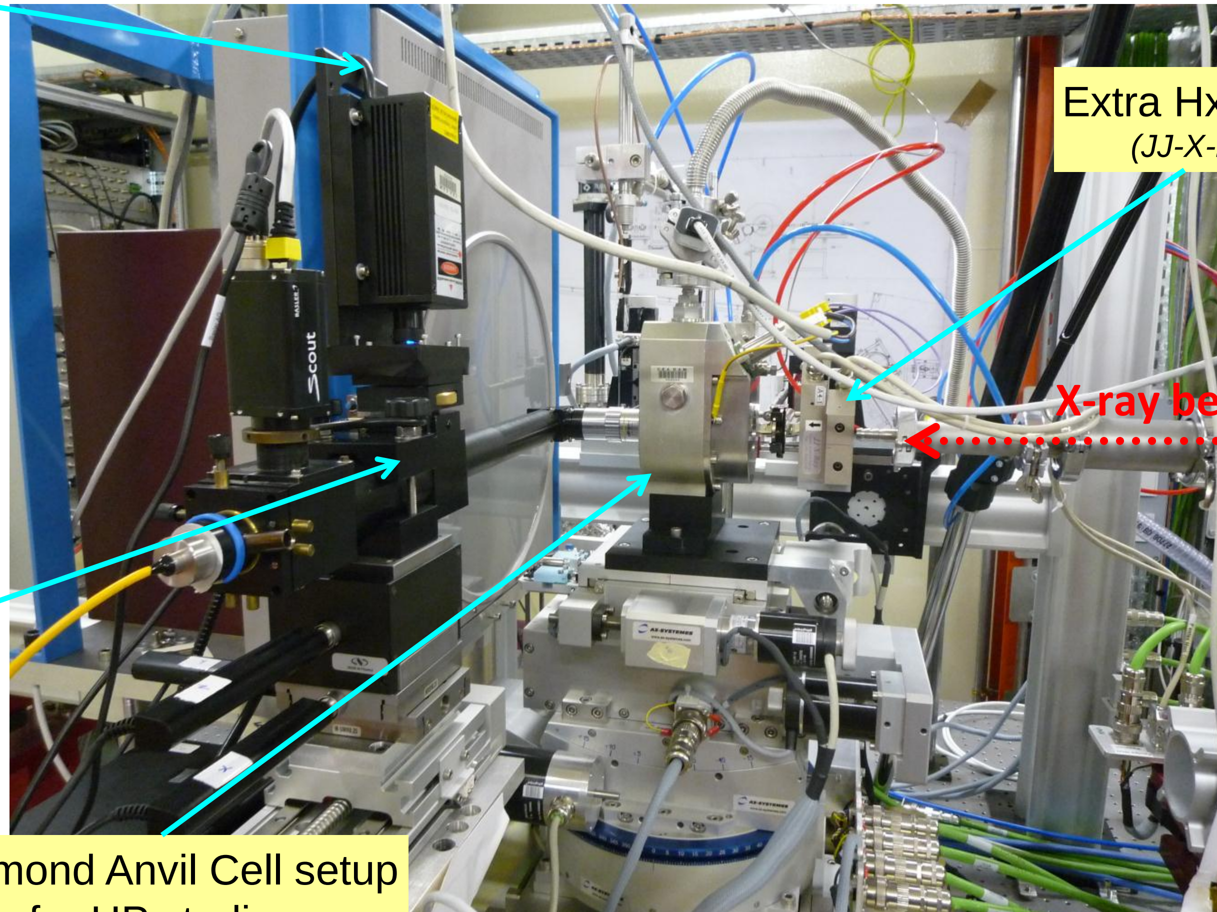
Highly rigid experimental table
with micrometric elevation
*A-Z Systèmes Company (France) + Newport Bread Board*

Intensity monitors with Si-diodes
*(Soleil home-made)*

# Station B: Transmission XRD set-up

2D-image plate detector
*Marresearch GmbH (Germany)*

Extra HxV slits
*(JJ-X-ray)*

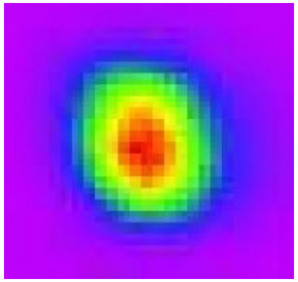



Optical microscope

Diamond Anvil Cell setup for HP studies

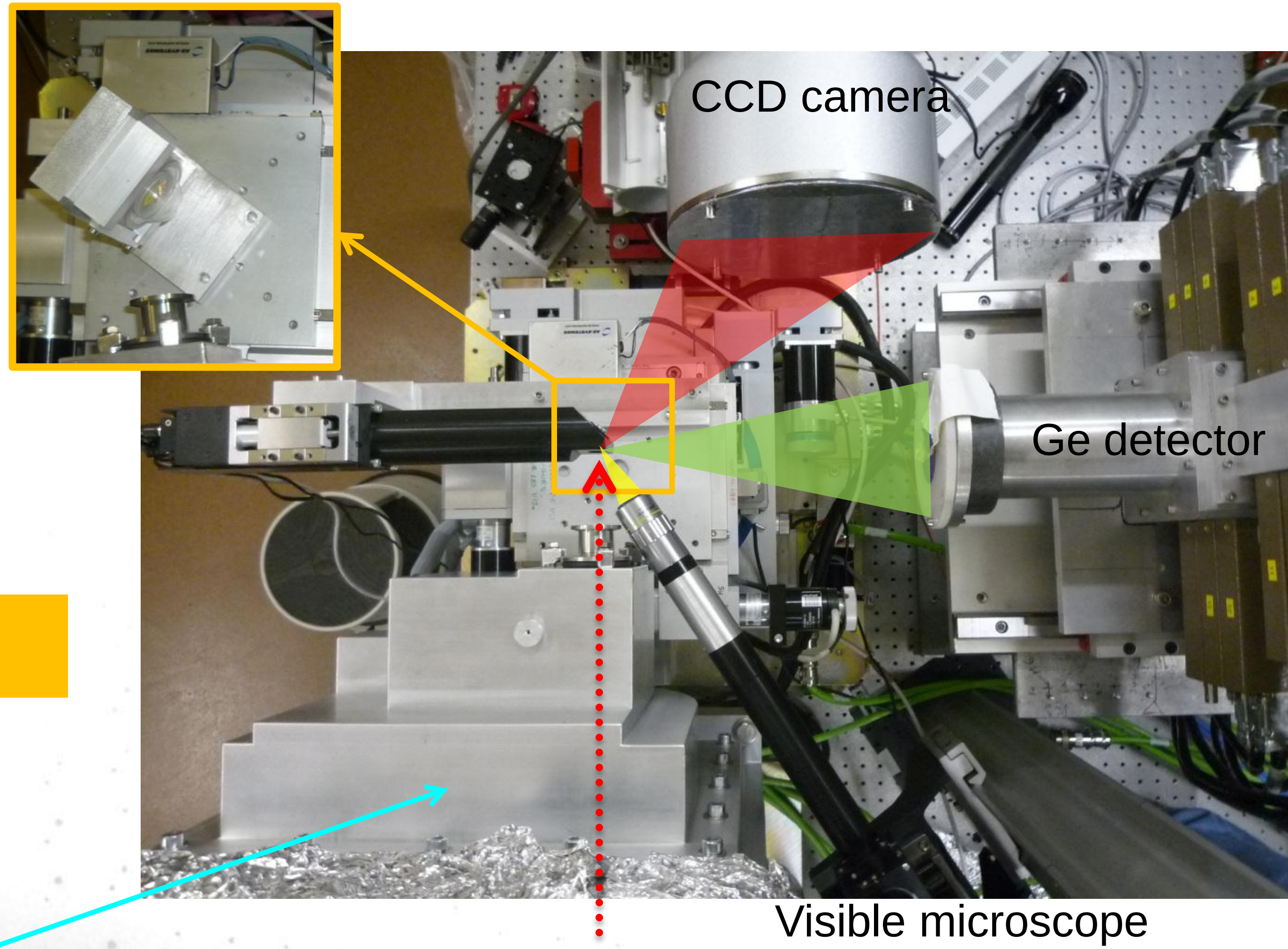
Collimated beam:
~ 50 x50 µm$^2$

# Station B: Micro-beam setup with K.B. optics



Typical Beam size
(FWHM H x V )
**10 x 10 µm²**

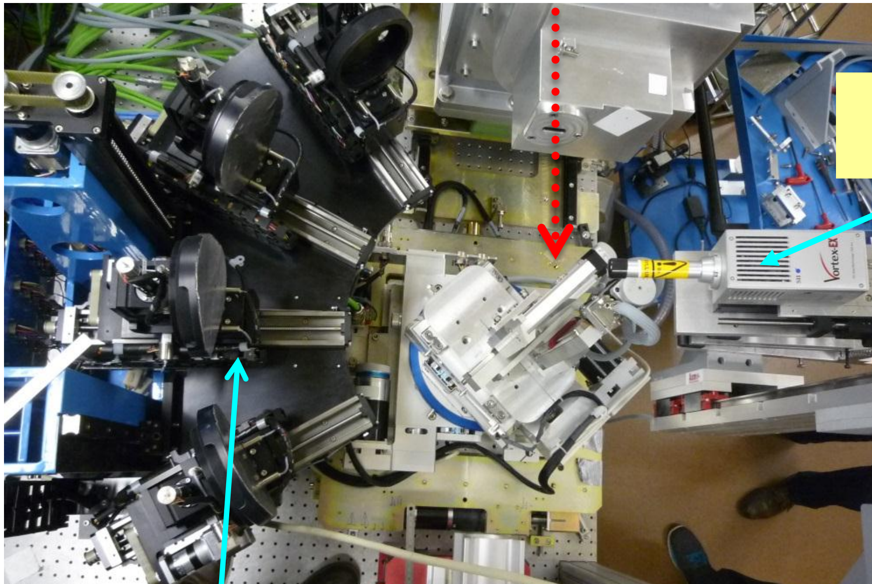
Flux
$1.10^{10}$ ph/s at 8 keV




**X-ray microbeam**

Additional microfocusing optics

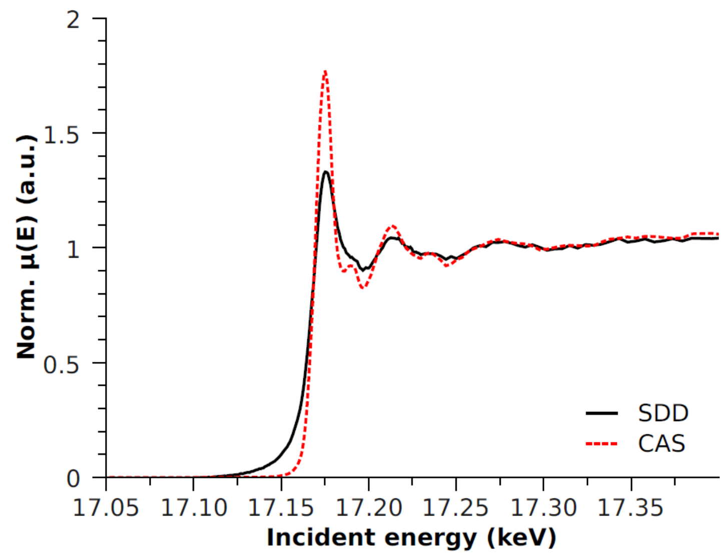
# Station B: X-ray Emission Spectroscopy set-up




*in collaboration with Fame CRG @ESRF, Grenoble*

## High-Energy Resolution XAS

**U $L_3$-edge measurement**

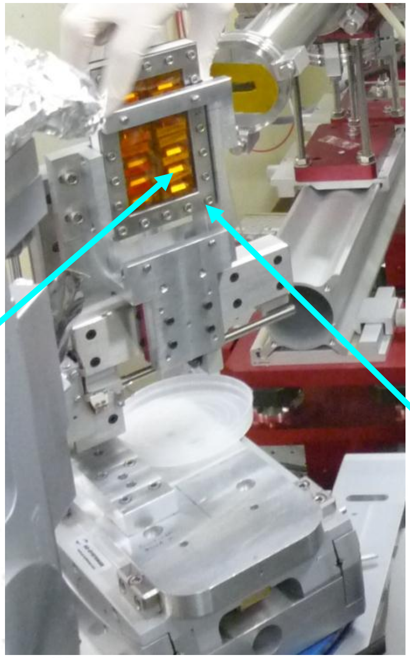


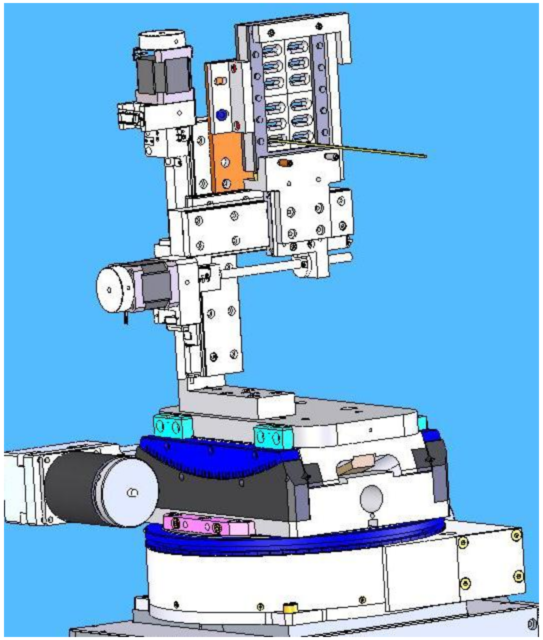
# Sample environment

# Standard sample environments for XAS

**Specific motorized stage**
**for multi-sample holder**
available in July 2010

*Supported by*





Multi-sample cell
for liquids
*(CEA Marcoule)*

Multi-sample cell
for solids
*(Soleil)*

# Sample-holder for diluted solutions

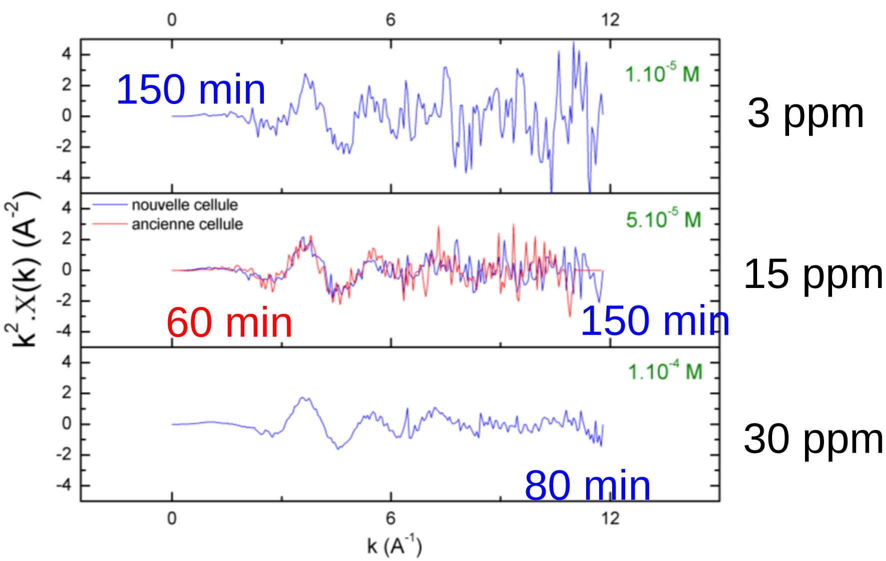
*Collaboration with Ch. Den Auwer et al. (U. Nice)*

Development of a special cell adapted for XAS measurements in fluorescence mode for highly diluted solutions (ppm scale)

Supported by

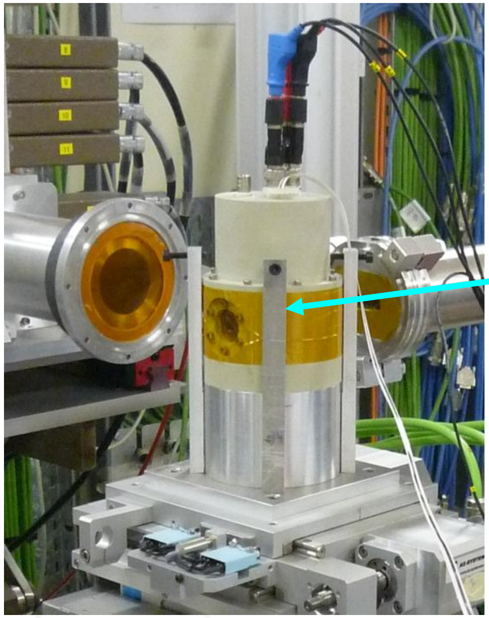
NEEDS

Results of first tests on Yttrium solutions (K edge 17038 eV close to actinides) with prototype cell (beginning of 2013)

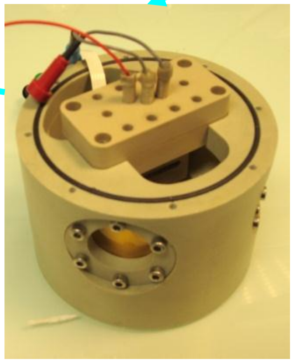


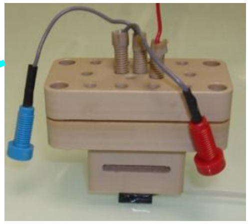
# Electrochemical cell for radionuclide solutions

***Collaboration with M. Schlegel, M. Tabarant et al. (CEA Saclay)***



Experimental setup on the beamline

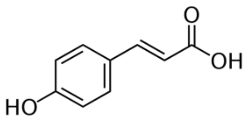




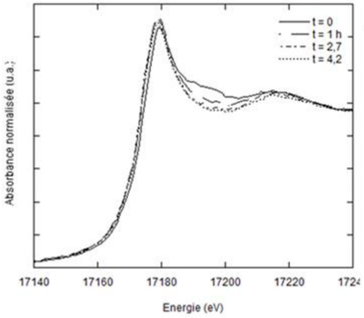
Special doubly-confined spectro-electrochemical cell
with low volume (1ml) for XAS in transmission and fluorescence

*Supported by*

**First investigations on uranium in paracoumaric acid medium**
(mimetic compounds of humic acids )




Paracoumaric acid

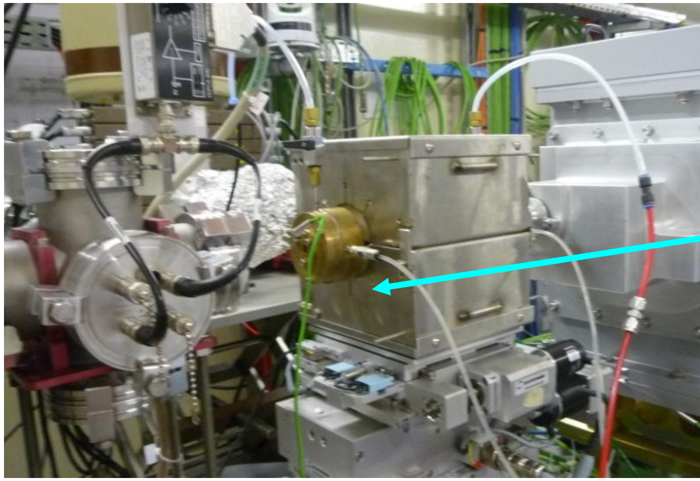



- 70 % of uranium (VI) reduced
- Formation of U(IV) - PCA complex rather than $UO_2$

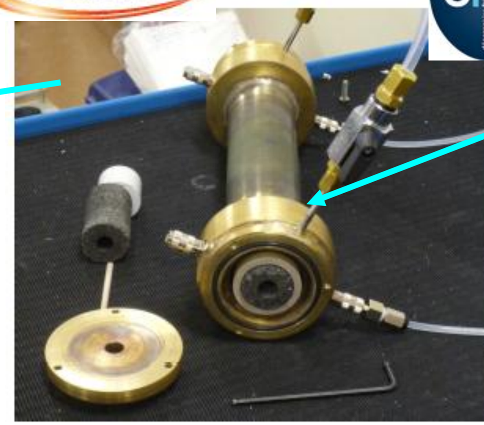
http://www.synchrotron-soleil.fr/portal/page/portal/Soleil/ToutesActualites/2012/SpeciationActinides-MARS

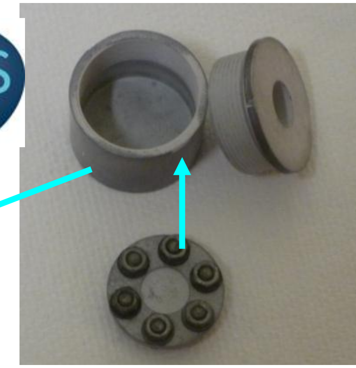
# High Temperature furnace for molten salt studies

*Collaboration with C. Bessada, L. Maksoud, D. Zanghi et al.*
*(CEMHTI CNRS-Orléans)*



**Special furnace for transmission XAS measurements**
**(conception by CEMHTI)**





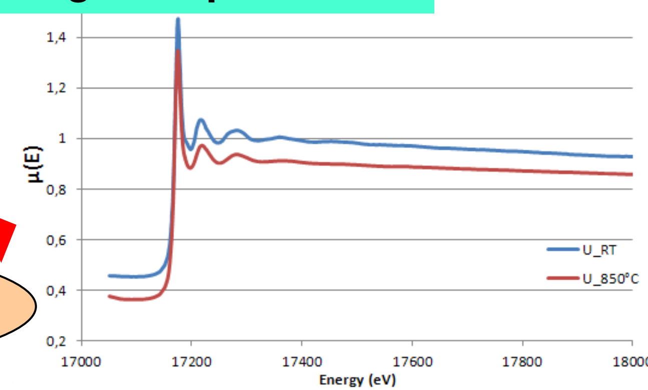
**Special doubly confined cell**
**(conception by CEMHTI)**
*Bessada et al., NEA Nucl. Sci. (2009)*
*Numakura et al., Prog. in Nucl. En. (2011)*

<u>Triple</u> confinement concept to avoid contamination at high temperature **(up to 1500°C)**

## Purpose: investigations of actinide molten salts at high temperatures

Study of actinide fluorides-alkali fluorides mixtures
=> involved in **pyrochemical processes for the recycling** of the spent fuels in GENIV new reactors concepts.
=> Linked to researches on the Th-U3 fuel **Molten Salts Reactors**.

March 2013: First measurements
on uranium molten salts !!!



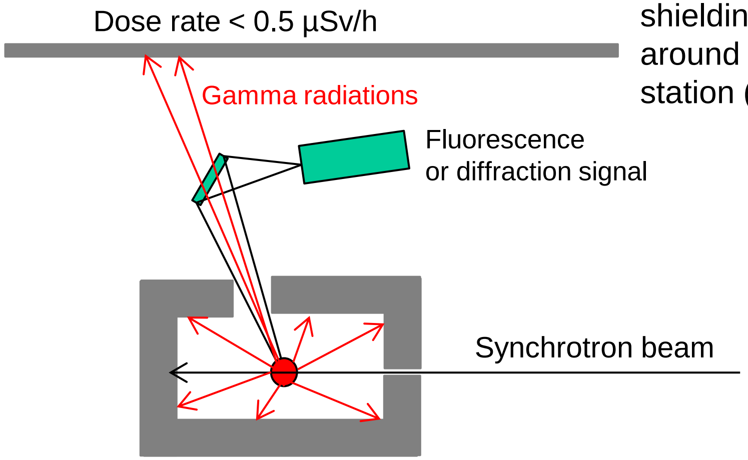
# Future equipment: shielding

## The benchmark sample

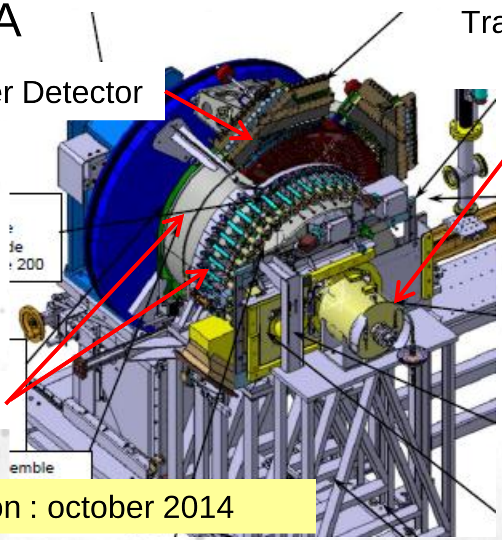
**After irradiation** PWR $UO_2$ fuel
Burn-up = 90 GWj/tMLi
Cooling = 1 year
mass = 23 mg
Total radioactivity = 3 GBq
Dose rate = 2 mSv/h at 30 cm

**Mechanical design realized by CEA**
**Nature of shielding defined by CEA**
**and confirmed by SOLEIL**

## General principle

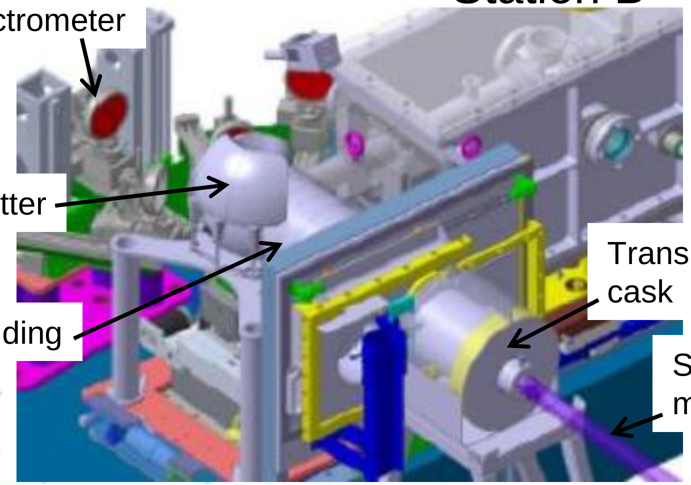



## Station A




Installation : october 2014

## Station B

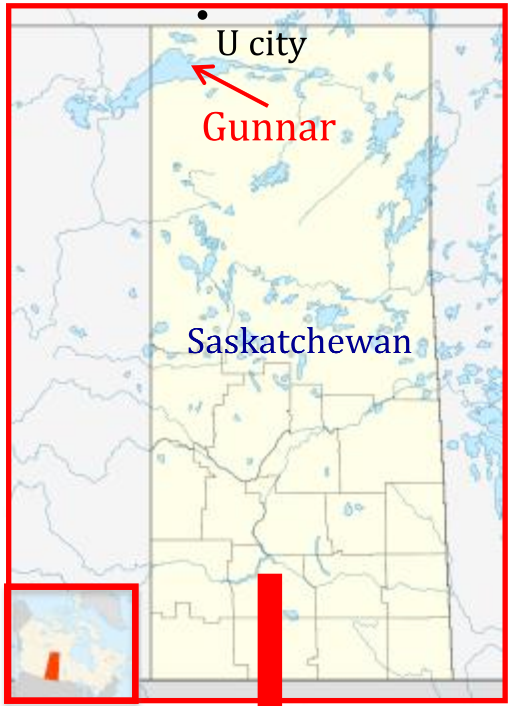


# Examples
# of recent results

# Speciation of uranium in mill tailings from Gunnar (Canada)

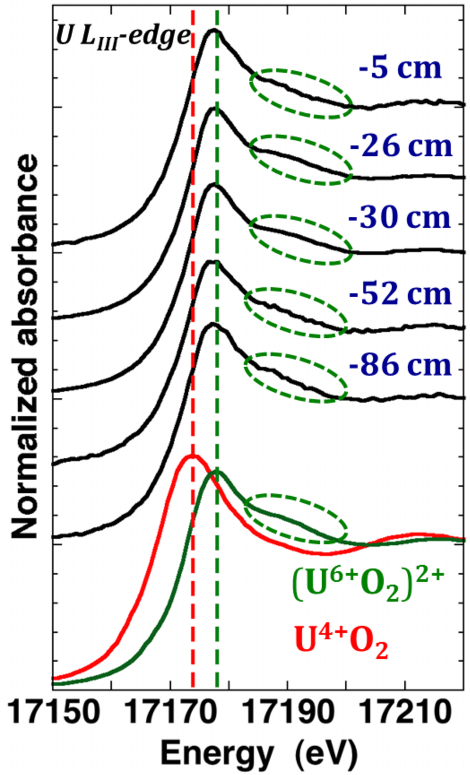
*Project by : G. Othmane, T. Allard, G. Morin (CNRS/U. Paris) et al.*

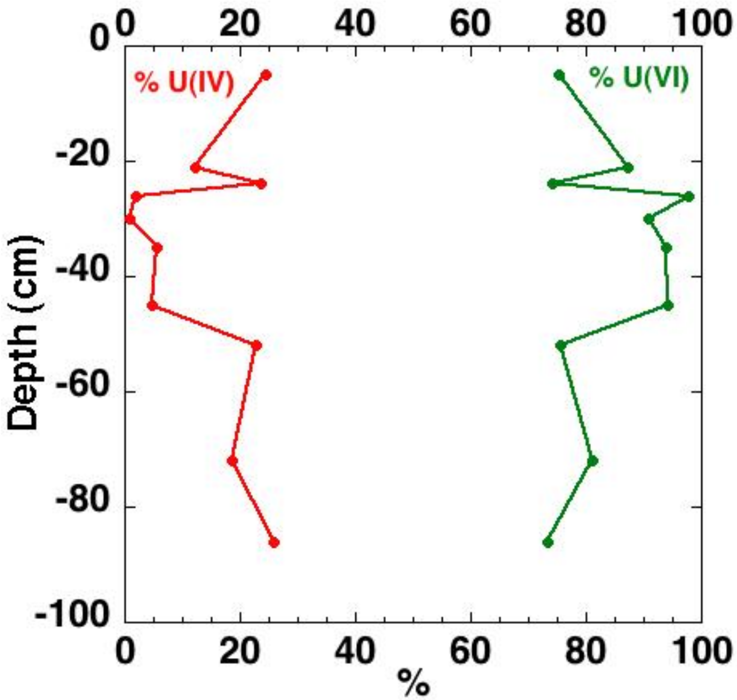
*Environmental Science & Technology, **2013**, 47(22): 12695–12702*




**4.4 million tons of U mill tailings**

**Objectives: investigate U speciation in Gunnar tailings** in order to determine the processes controlling uranium trapping



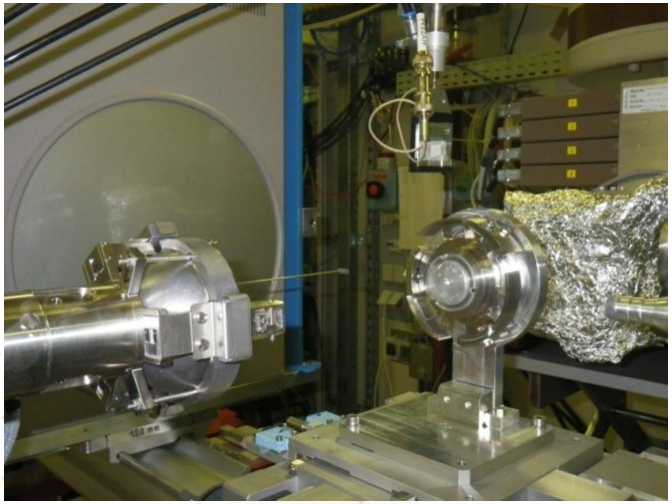

$UO_2^{2+}$ predominance

# Analysis of Oxides Dispersion Strengthened steel by XAFS

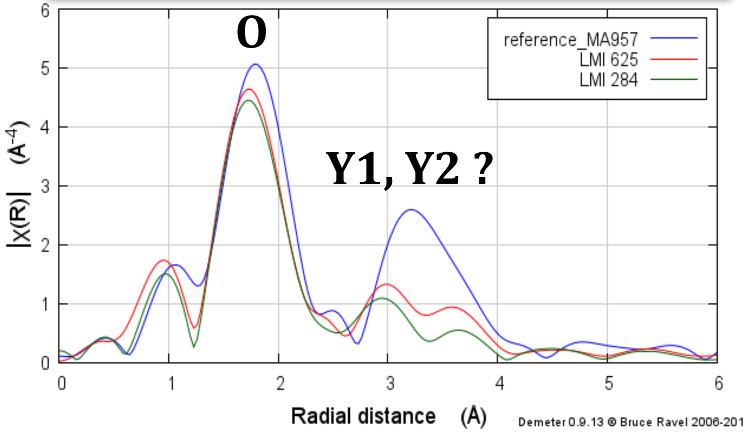
*Project by : D. Menut , J.L. Béchade (CEA Saclay) et al.*

ODS materials are promising candidates for structural components of GEN IV and fusion reactors.
The study is aiming at characterizing the nano-particles dispersed in ODS steel reinforced by $Y_2O_3$ (up to 0.6 Wt%) **after neutron-irradiation** up to high irradiation dose in Sodium cooled Fast Reactors and Pressurized Water Reactor.

**This was the first experiment on samples with an activity higher than the exemption limit.**



**Fourier-transformed EXAFS spectra**




EXAFS: Several structure may be found in clusters: $Y_2Ti_2O_7$, $Y_2O_3$, $YTiO_3$, $Y_2TiO_5$

**NEUTRON IRRADIATION CONDITIONS:**
(same d.p.a., Higher neutron energy in Supernova)

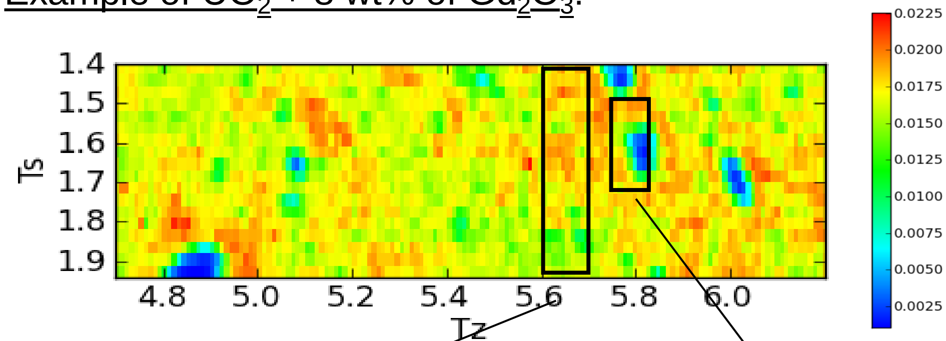
**LMI625 at Supernova (Phenix); LMI284 at Alexandre (OSIRIS)**

# Microstructural analysis of (U,Gd)O2 nuclear fuel

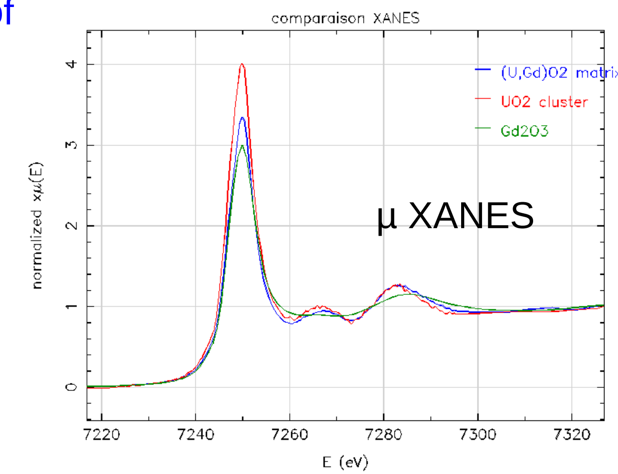
*Project by : R. Delorme , Ph. Martin , Ch. Valot , (CEA Cadarache) et al.*

Background: understanding structural and microstructural *heterogeneity* of $(U,Gd)O_2$ nuclear fuel behaviour under irradiation.

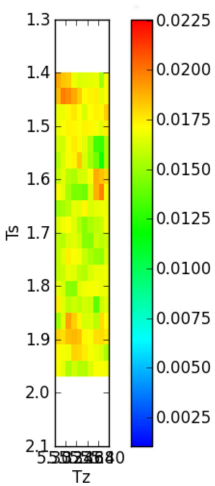
Example of $UO_2$ + 8 wt% of $Gd_2O_3$:

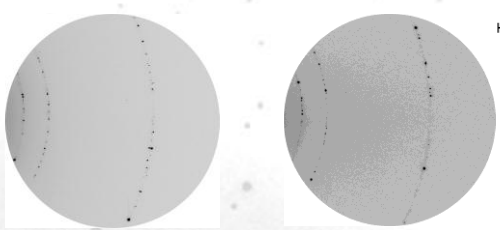



→ XRF & XRD at 8 keV with 10*10 µm² beam.



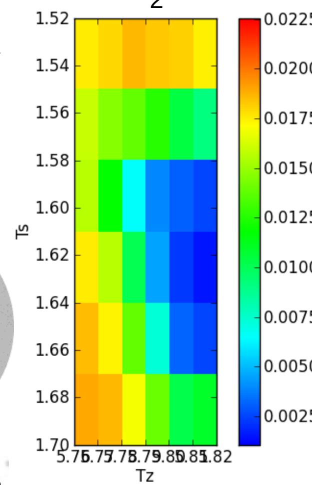

$(U,Gd)O_2$ matrix

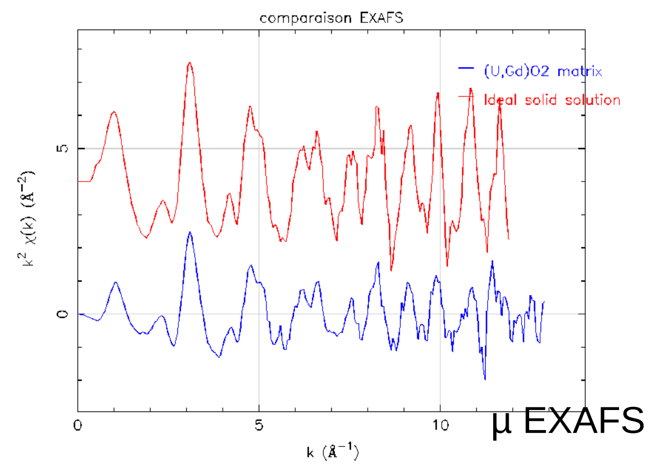


Both zones have a fluorine type crystallographic structure

$UO_2$ cluster

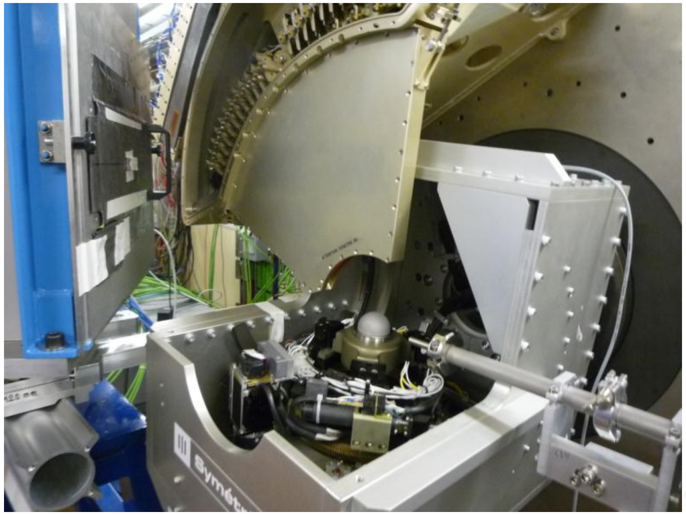


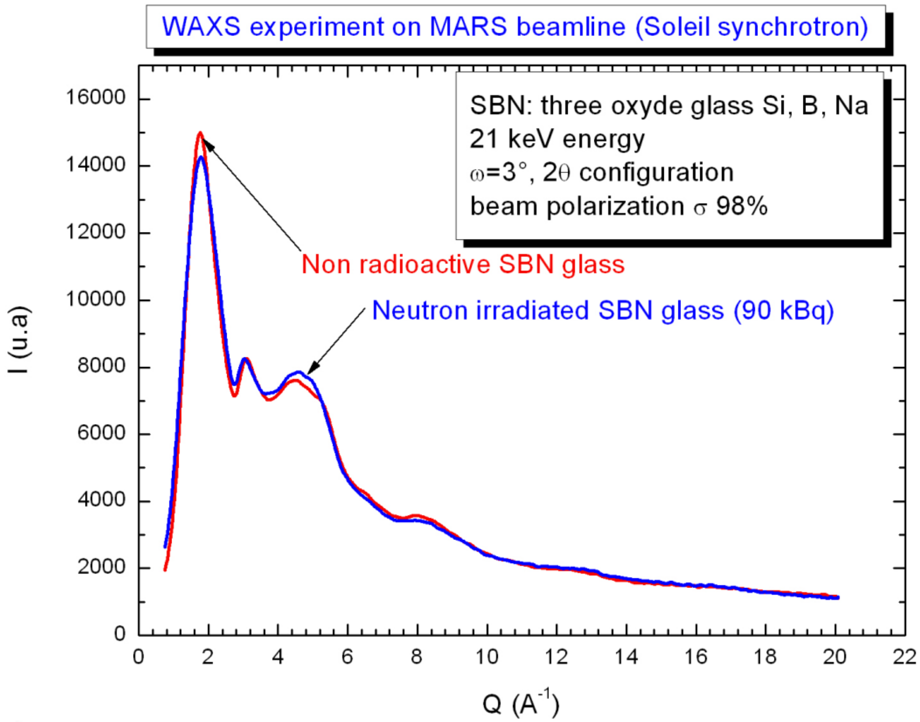
# Investigation of irradiated glasses by WAXS

*Project by : O. Bouty, S. Peuget (CEA Marcoule) et al.*

The objective of this experiment is to determine the X-ray structure factor of a borosilicate glass homogeneously irradiated by neutrons in the OSIRIS reactor



- 21 keV
- Beam size macrobeam
- Flux ~ 1.8 $10^{11}$ ph/S



# Summary

## Current situation:

Beamline is operational with both XAS station and HRXRD stations using a macrofocused beam (400x300µm$^2$) or microfocused beam (10x10µm$^2$)

Experiments are possible and authorized for samples
**with activities < 20 000 x exemption limit**
**(isotopic dependent and only at ambient T and P)**

## For next years (2015-2016):

Beamline should be opened for samples
**with activities < 200 x exemption limit (HP, HT, LT, …)**
**with activities < 2 10$^6$ x exemption limit (ambient T and P)**

## To apply for beamtime:

Standard proposal submission of SOLEIL (2/3 of the beamtime)
Dead lines : February 15th and September 15th
Travel expenses and accommodation covered by SOLEIL for 3 French users and only 2 European users
http://sunset.synchrotron-soleil.fr/sun/

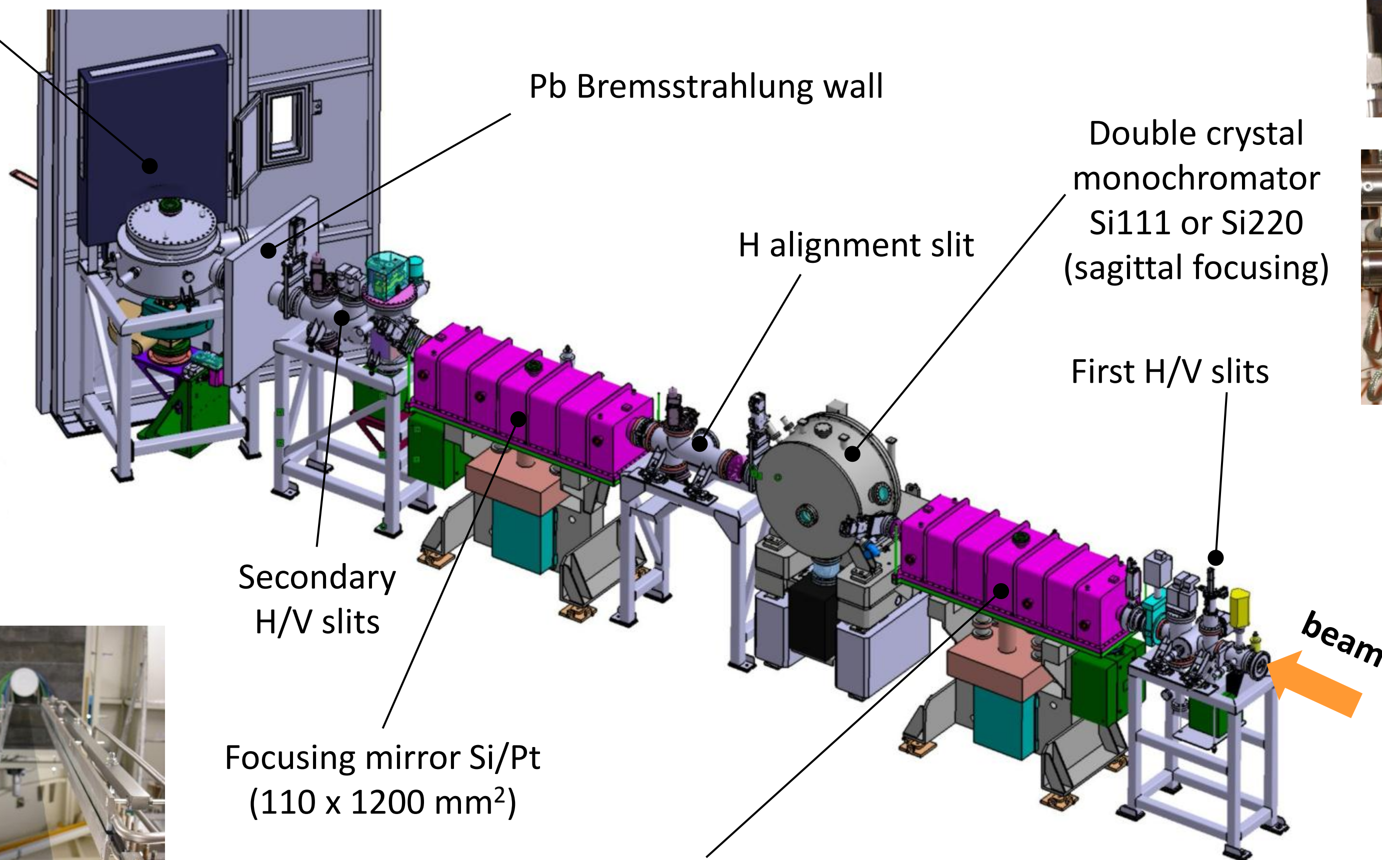
# Acknowledgements

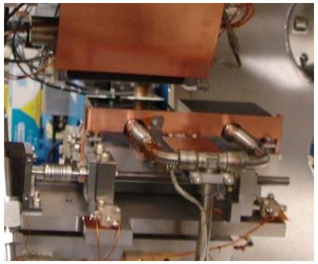
Thanks to SOLEIL Staff (mechanics, optics, software, electronics, safety…)

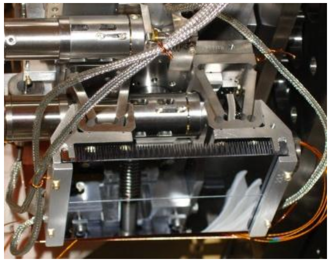
**THANKS A LOT to our USERS (CEA, CNRS,…)**

Bruno Sitaud
Beamline responsible
(2004-2013)

# Optics equipment





# Autorizations for radioactive samples

Since mid-2010: Experiments possible only for samples
**with activities < exemption limit (isotopic dependent)**
*for U238 => 10 000 Bq (~ 800 mg)*
*for Pu239 => 10 000 Bq (~ 4 µg)*

Since september 2013: Experiments possible for samples
**with activities < 20 000 x exemption limit**
**(isotopic dependent and only at ambient T and P)**
*for U238 => 200 000 000 Bq (~16 kg)*
*for Pu239 => 200 000 000 Bq (~87 mg)*

2015-2016: Autorisations for samples
**with activities < 200 x exemption limit (HP, HT, LT, …)**
**with activities < 2 $10^6$ x exemption limit (ambient T and P)**

| | | Technological fields | | | | |
|---|---|---|---|---|---|---|
| Radioactive classes of samples | | F0 | F1 | F2 | F3 | F4 |
| | C0 (A <1 ET) | | | | | |
| | C1 (A <200 ET) | | | | | |
| | C2 (A <2 $10^4$ ET) | | | | | |
| | C3 (A <2 $10^6$ ET) | | | | | |

**Technological fields that have been considered :**
F0 = ambient conditions
F1 = high P (100 GPa)
F2 = low T (10 K)
F3 = chemical reactions
F4 = high T (1800 K)