

DE LA RECHERCHE À L'INDUSTRIE

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# CHARACTERIZATIONS AND TREATMENT TESTS OF GRAPHITE WASTE FROM FRENCH GAS-COOLED REACTORS

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*Work supported by Andra in partnership with CEA,  
CNRS/ENS and EDF*

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I – Nuclear graphite waste presentation

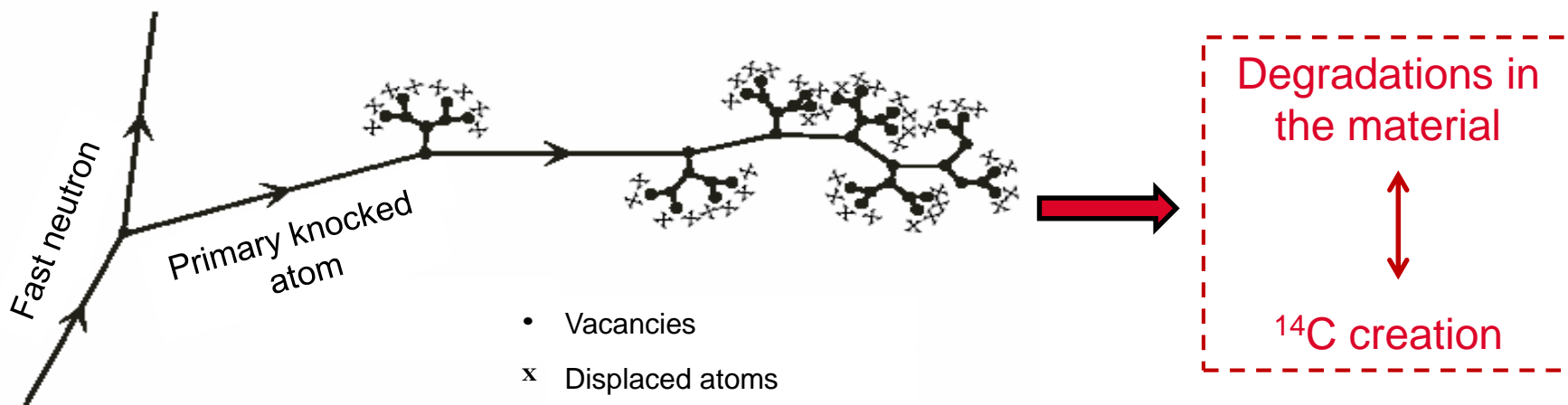
II – An original treatment proposition for  $^{14}\text{C}$  extraction

III –  $\text{CO}_2$  gasification treatment tests

### Graphite in French gas-cooled reactors

■ Neutron moderator in first generation of nuclear reactors

### Neutron irradiation



*Bonal, Gosmain, 2007*

### Consequences of dismantling

■ 23,000 tons of graphite waste will be generated in France (250,000 tons at the world scale)

■  $^{14}\text{C}$  and  $^{36}\text{Cl}$  are still active after a thousand years

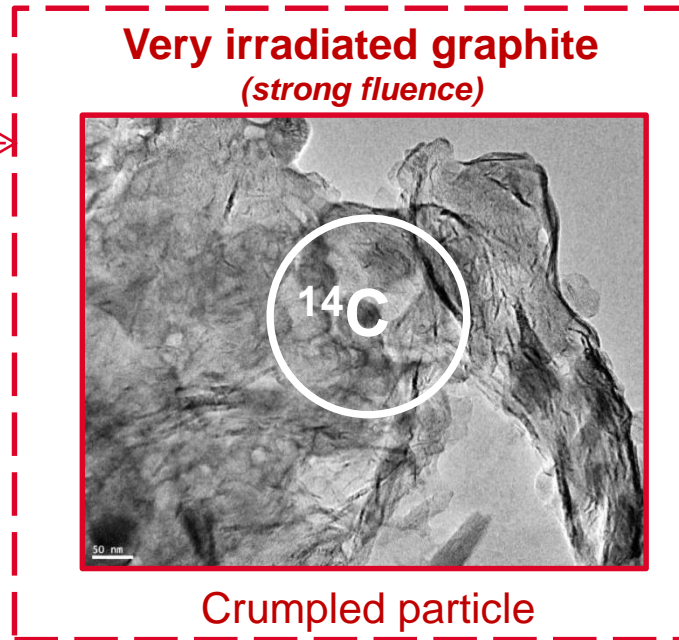
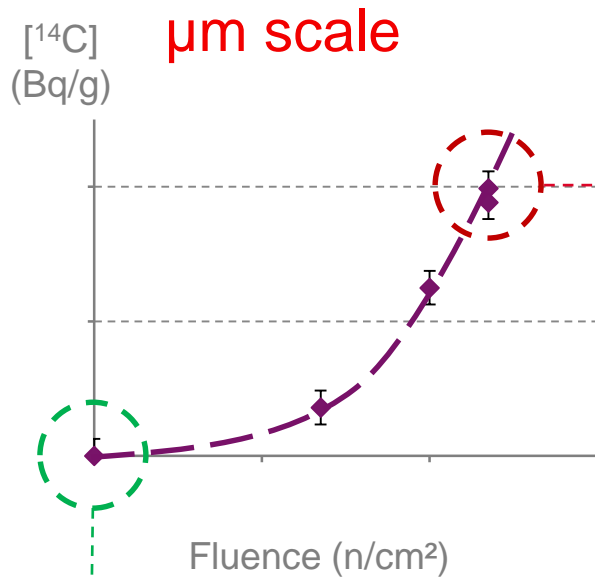
■  $^{14}\text{C}$  will be the main contributor to the activity

■ Our aim: to reduce  $^{14}\text{C}$  concentration of graphite waste

# I – GRAPHITE WASTE

□ CONTEXT

■ NEUTRON IRRADIATION EFFECT

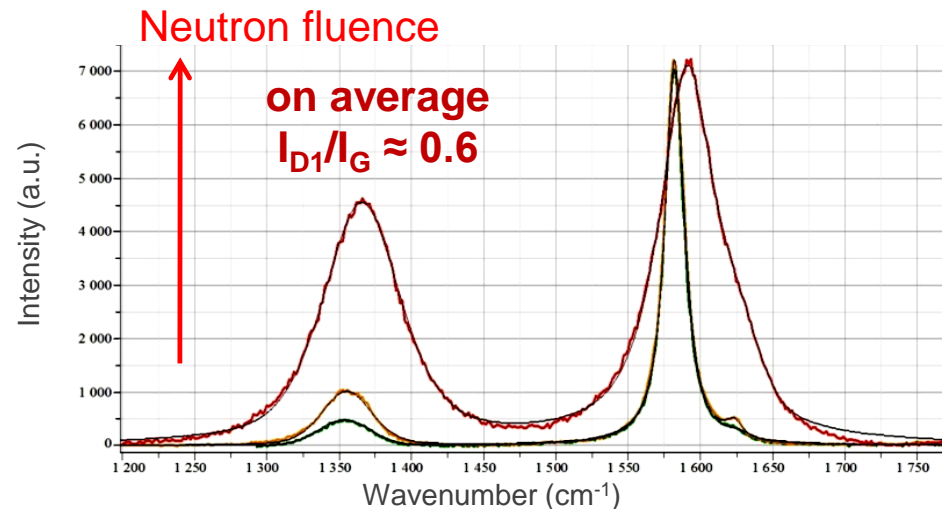
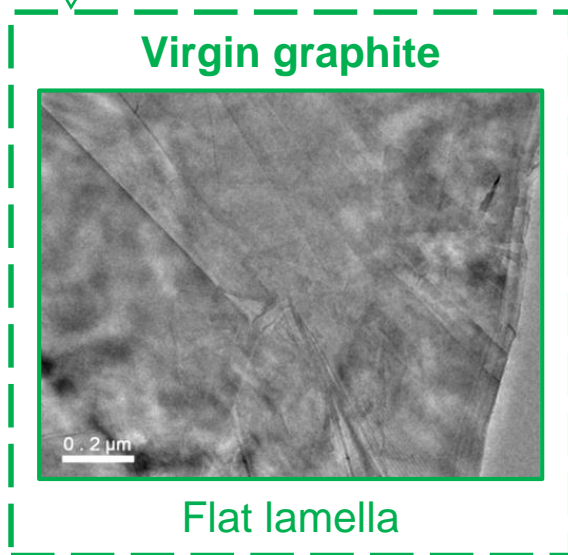


Rouzaud et al., Carbon 2011, 2012  
Pageot et al., 2016

With neutron fluence:

$I_{D1}/I_G$  increasing

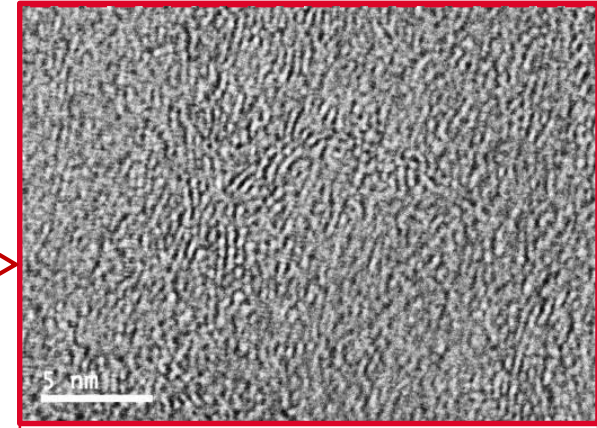
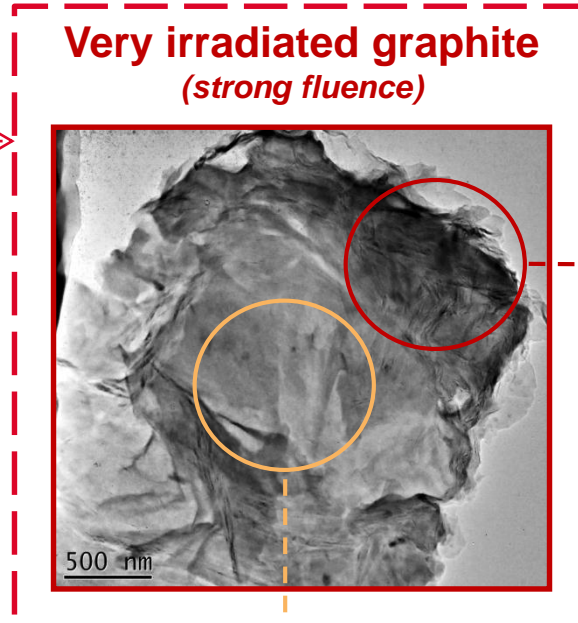
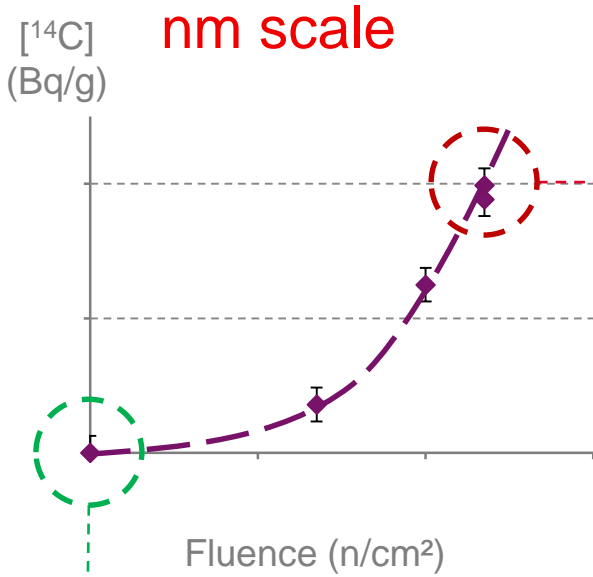
$[^{14}\text{C}]$  increasing



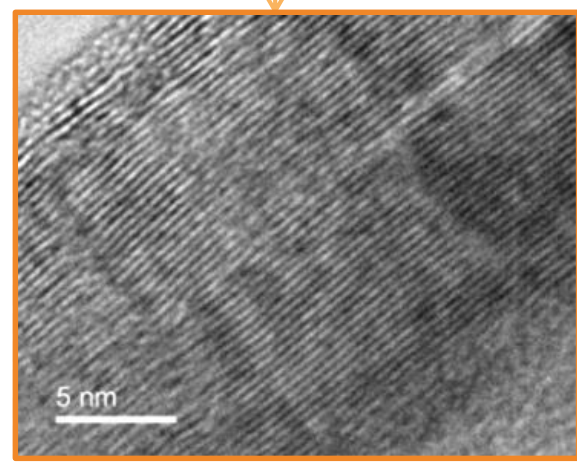
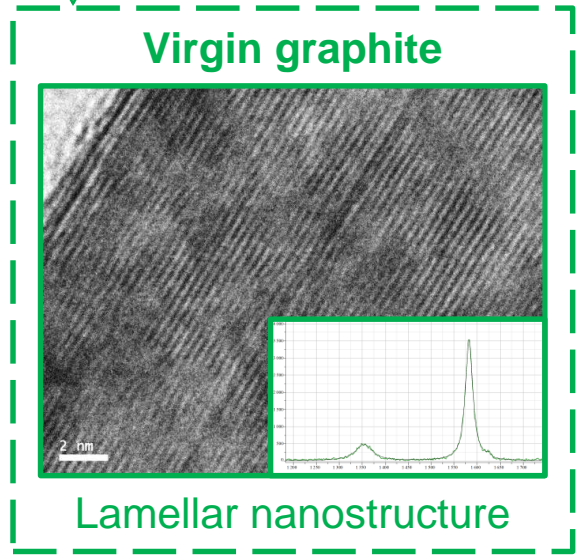
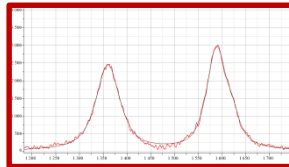
# I – GRAPHITE WASTE

□ CONTEXT

■ NEUTRON IRRADIATION EFFECT



Occurrence of nanoporous nanostructure  
 $I_{D1}/I_G \approx 0.9$



Preserved lamellar nanostructure  
 $I_{D1}/I_G \approx 0.4$

The Raman spectrum shows two peaks: a G band at approximately 1580 cm<sup>-1</sup> and a D1 band at approximately 1350 cm<sup>-1</sup>. The G band is significantly more intense than the D1 band.

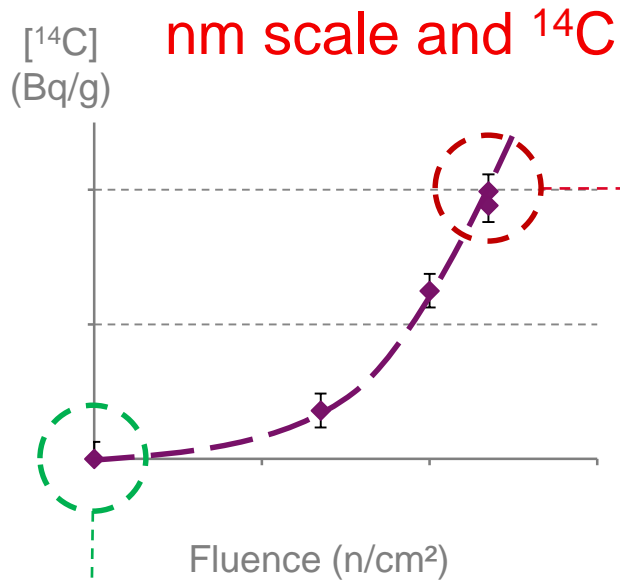
Pageot et al., 2016



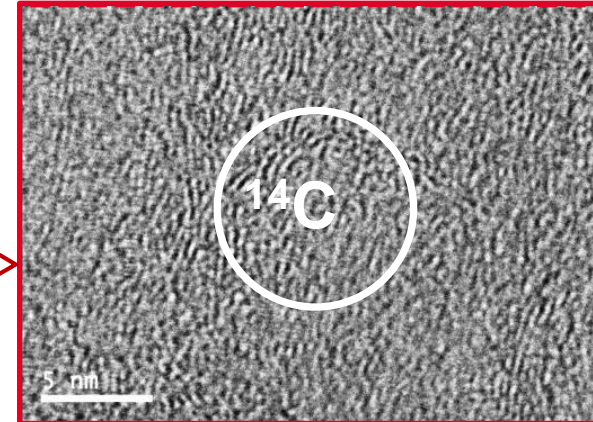
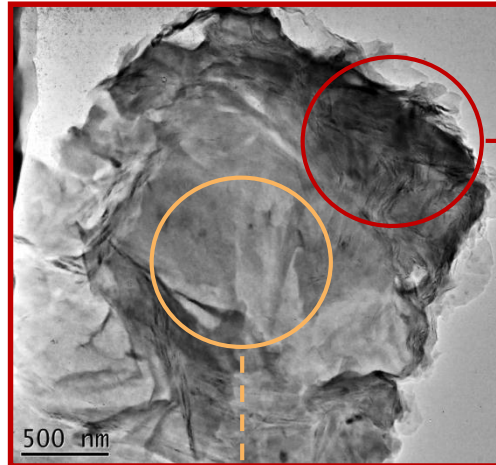
# I – GRAPHITE WASTE

□ CONTEXT

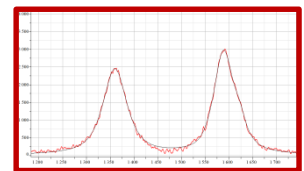
■ NEUTRON IRRADIATION EFFECT



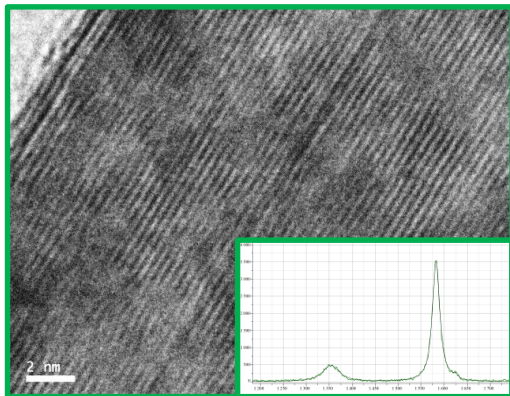
Very irradiated graphite  
(strong fluence)



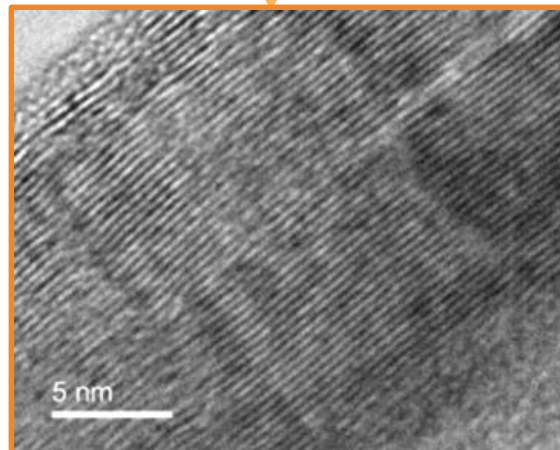
Occurrence of nanoporous nanostructure  
 $I_{D1}/I_G \approx 0.9$



Virgin graphite

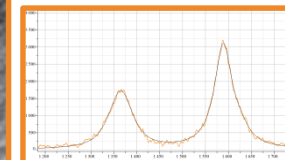


Lamellar nanostructure



Preserved lamellar nanostructure

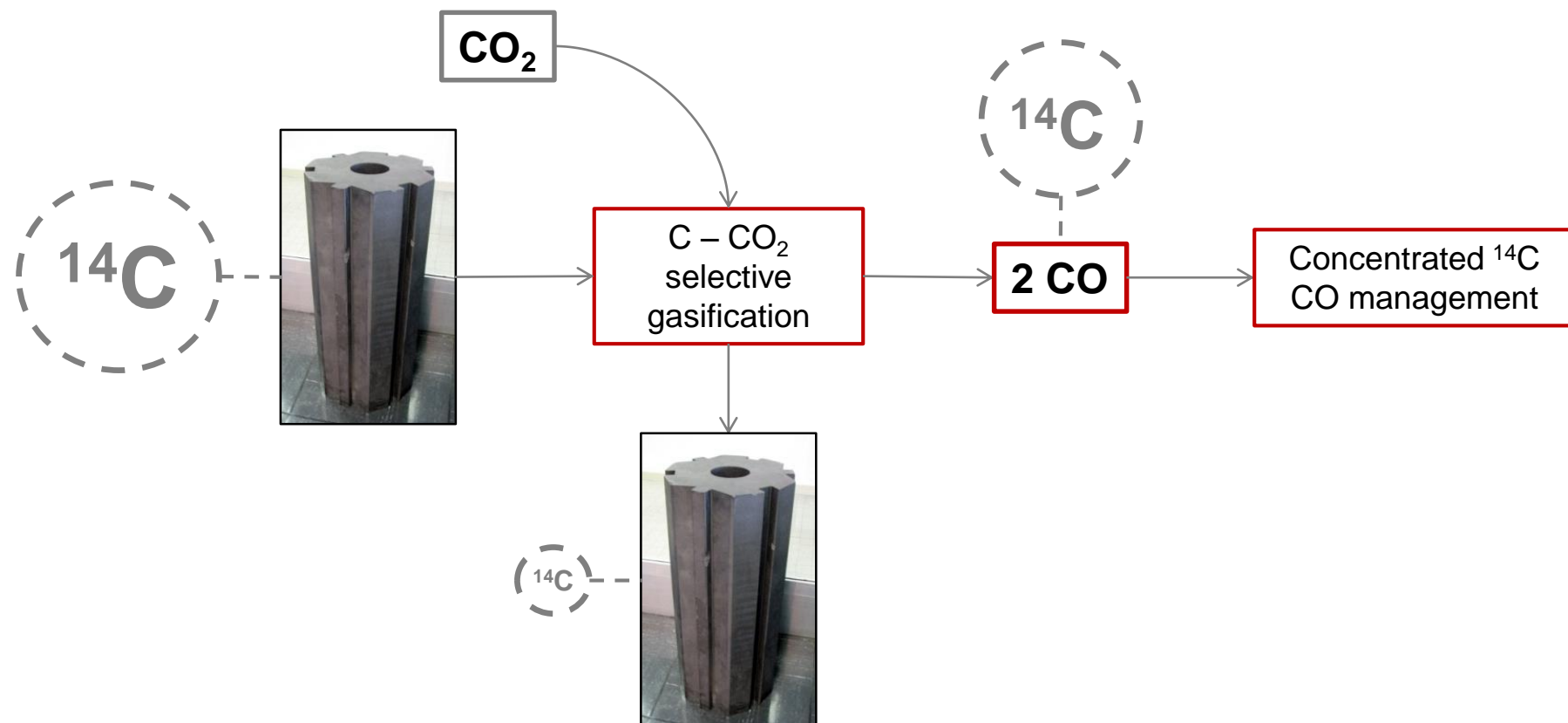
$I_{D1}/I_G \approx 0.4$



Pageot et al.,  
2016

### Graphite waste CO<sub>2</sub> gasification treatment proposition

■ Treatment principle and global vision of the <sup>14</sup>C management

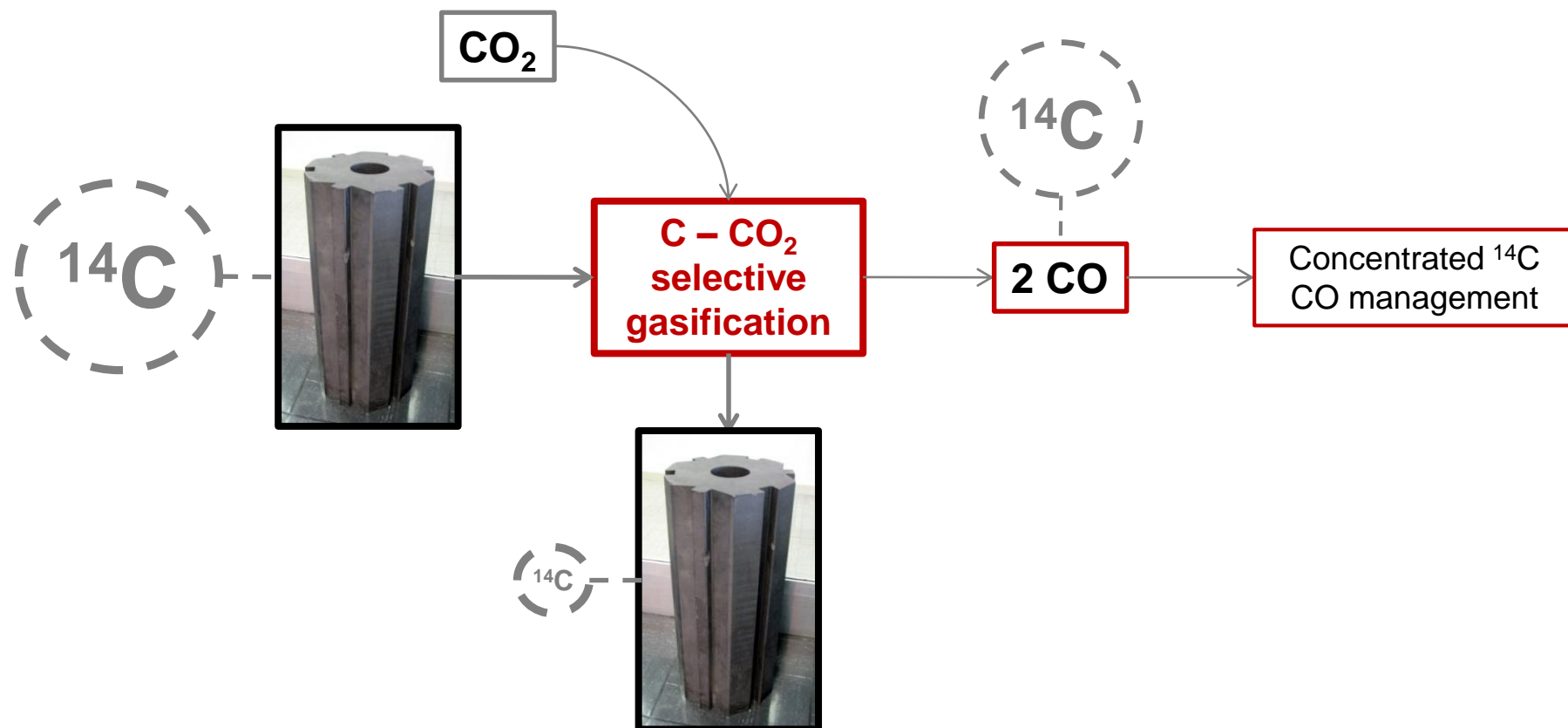


■ To selectively extract <sup>14</sup>C from graphite stacks with the lowest weight loss as possible

■ To concentrate <sup>14</sup>C into an insoluble carbon

### Graphite waste CO<sub>2</sub> gasification treatment proposition

- Treatment principle and global vision of the <sup>14</sup>C management



- To selectively extract <sup>14</sup>C from graphite stacks with the lowest weight loss as possible
- To concentrate <sup>14</sup>C into an insoluble carbon



## Nanostructure and C-CO<sub>2</sub> reactivity

Hypothesis on <sup>14</sup>C localization and nanostructure

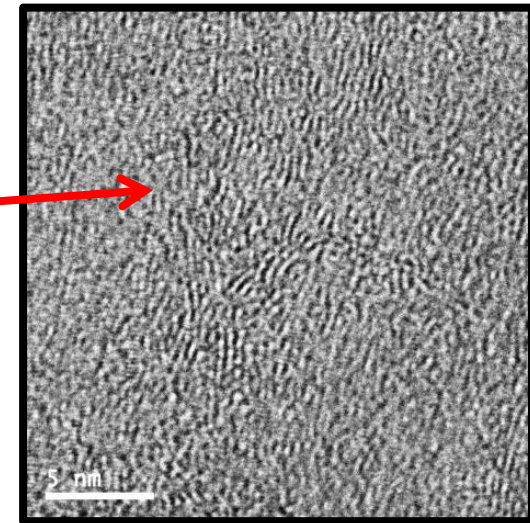
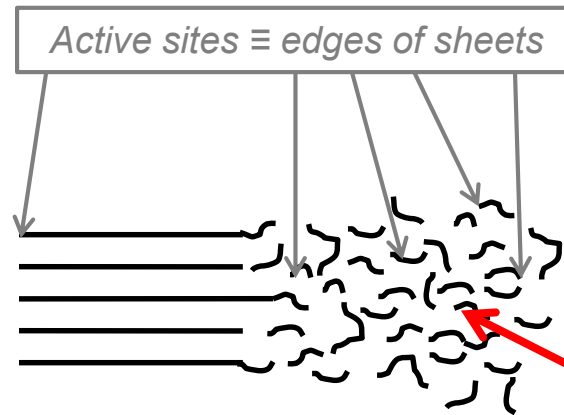
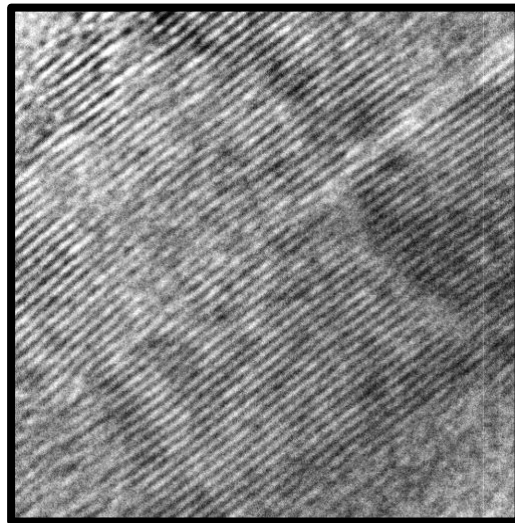


After irradiation

Rouzaud et al., Carbon 2011  
Moneger et al., Eurocarbon 1998  
Rodriguez-Reinoso et al., 1974  
Walker et al., 1959

Lamellar nanostructure <sup>14</sup>C

<sup>14</sup>C Nanoporous nanostructure



Low active site density

High active site density

Micrometer sized pores

Nanometer sized pores

Lamellar and nanoporous areas are deeply associated at the nanostructure scale.

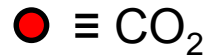
Hypothesis: <sup>14</sup>C should be localized into nanoporous areas.

## Nanostructure and C-CO<sub>2</sub> reactivity

Reactivity according to the nanostructures



Gas – carbon reaction

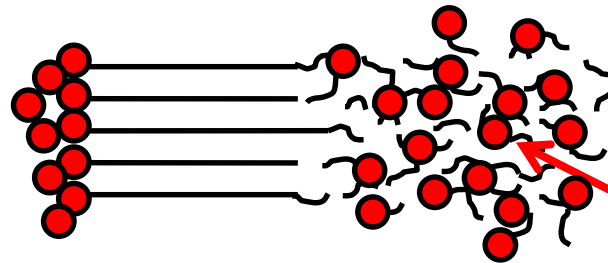
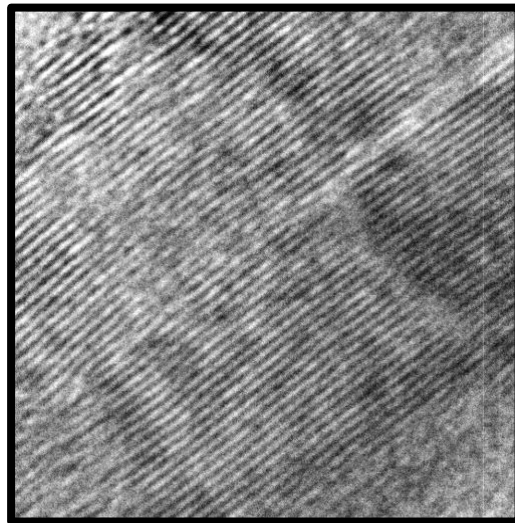


At constant local pressure

*Rouzaud et al., Carbon 2011*  
*Moneger et al., Eurocarbon 1998*  
*Rodriguez-Reinoso et al., 1974*  
*Walker et al., 1959*

Lamellar nanostructure <sup>14</sup>C

<sup>14</sup>C Nanoporous nanostructure

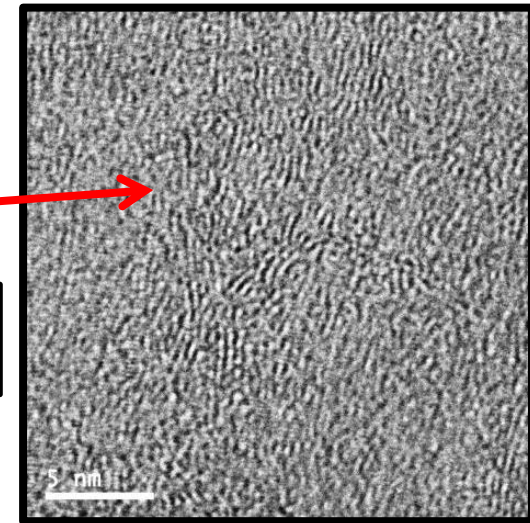


Shocks CO<sub>2</sub> – active site low probability

Shocks CO<sub>2</sub> – active site high probability

Molecular diffusion

Knudsen diffusion



- C-CO<sub>2</sub> reaction takes place on edges of graphene sheets and depends on active sites density.
- C-CO<sub>2</sub> reactivity also depends on the probability of shocks CO<sub>2</sub> – active site.

## Nanostructure and C-CO<sub>2</sub> reactivity

Selective reaction on nanoporous and <sup>14</sup>C rich areas

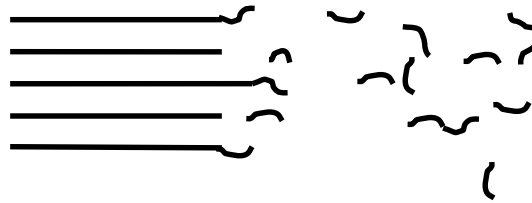
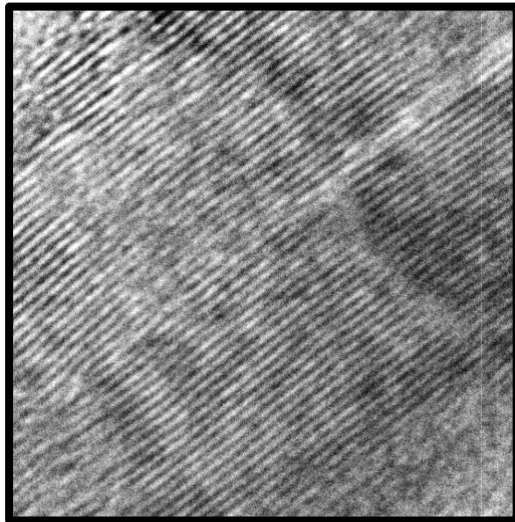
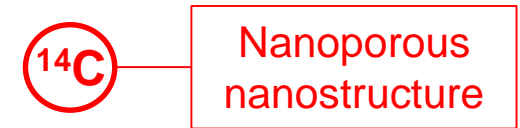


Gas – carbon reaction



At constant local pressure

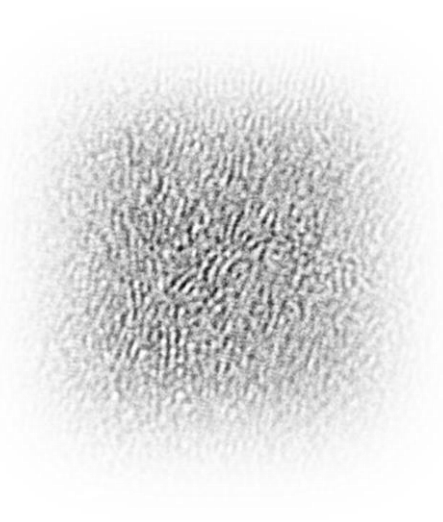
Rouzaud et al., Carbon 2011  
Moneger et al., Eurocarbon 1998  
Rodriguez-Reinoso et al., 1974  
Walker et al., 1959



Hardly reactive until 1000°C

reactive starting 900°C

Porosity opening and accessing to new active sites

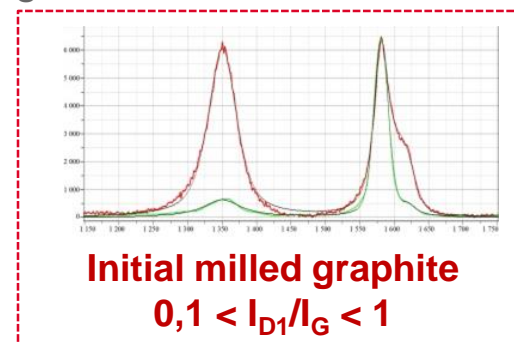
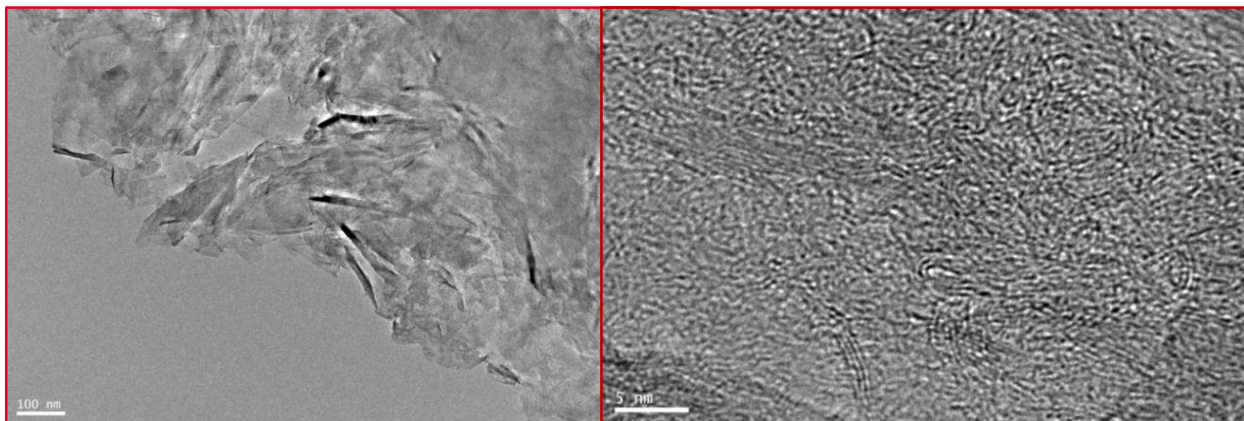


Neutron irradiated graphite partial gasification  
<sup>14</sup>C global concentration decrease



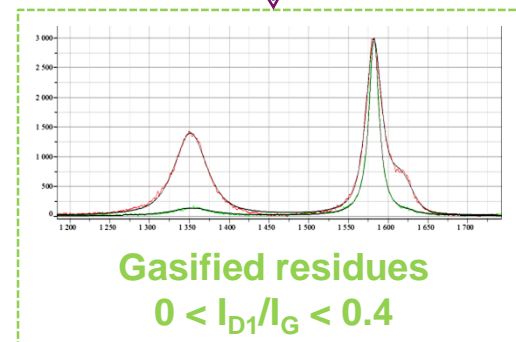
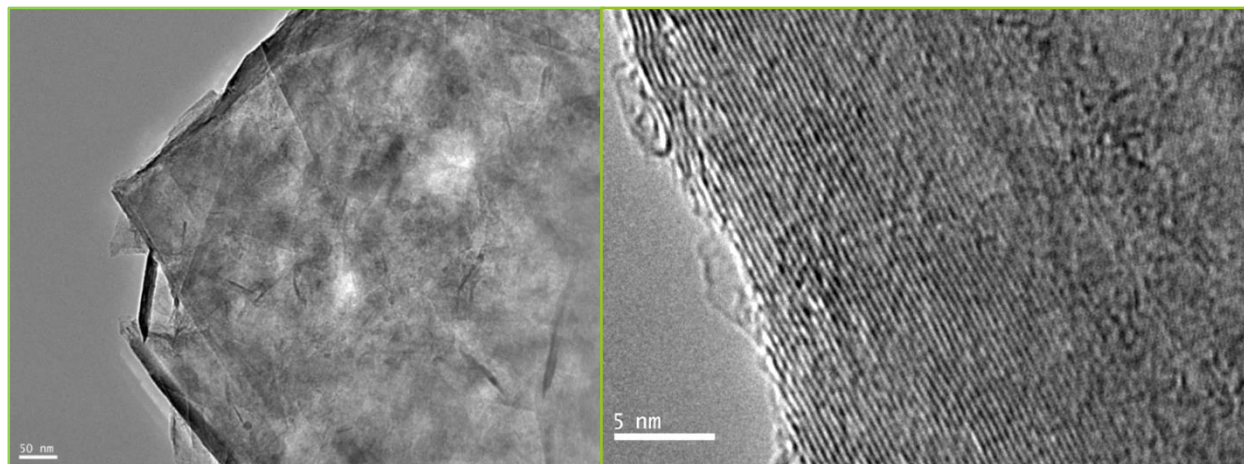
### Irradiated graphite analogue: milled graphite

- Similar structure (Raman, TEM) nanostructure (TEM) and heterogeneities
- Advantages: **non radioactive** and important available volume



*CO<sub>2</sub> gasification treatment*  
 **$T^{\circ}=950^{\circ}\text{C}$ ,  $p_{\text{CO}_2}=0.1 \text{ MPa}$ ,  $t=1\text{h}$**

**Weak relative weight loss**  
about **10 %**

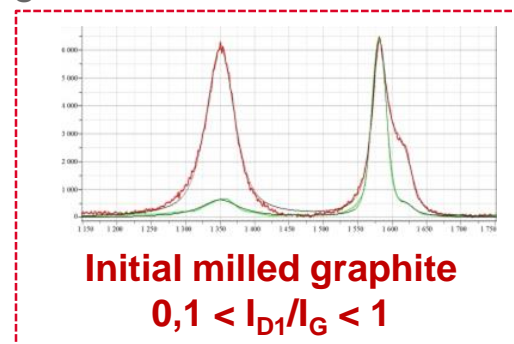
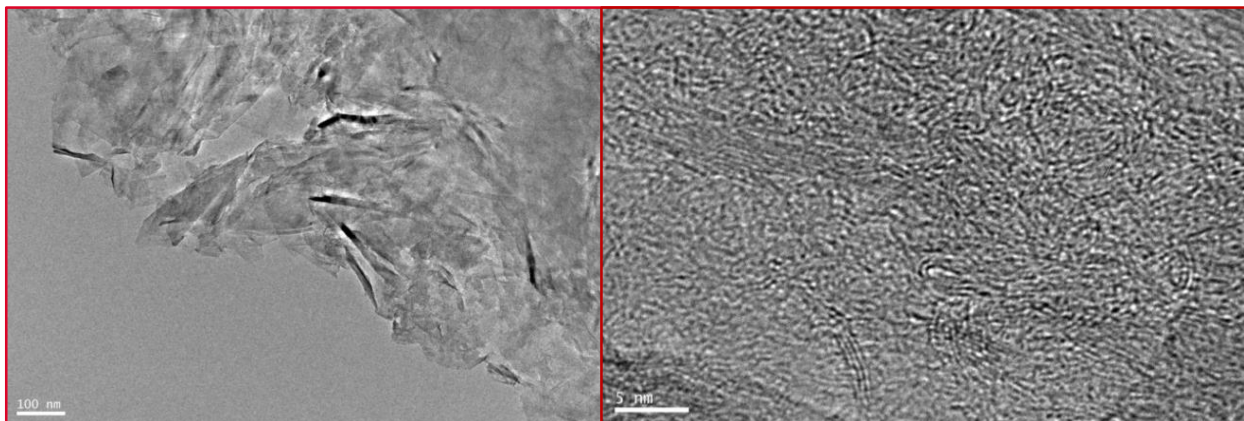


Pageot et al., 2015

Reactivity experiments carried out at the IS2M laboratory

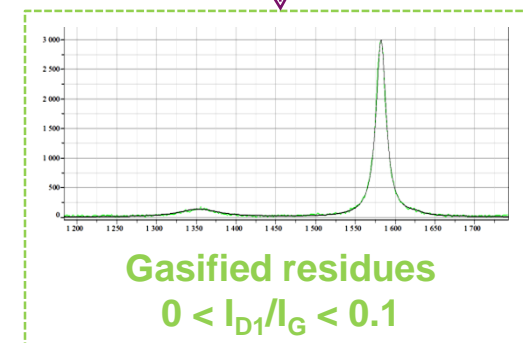
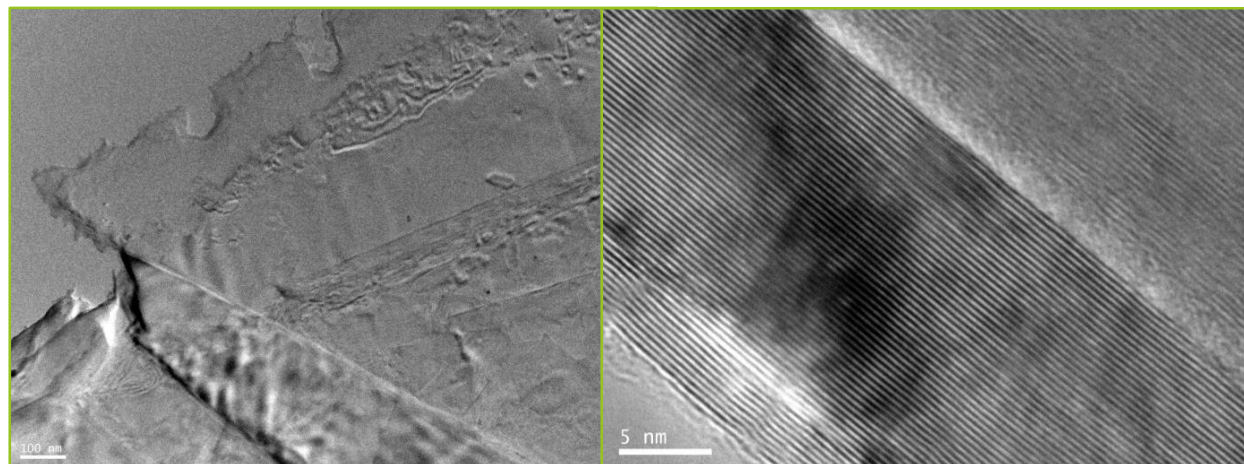
### Irradiated graphite analogue: milled graphite

- Similar structure (Raman, TEM) nanostructure (TEM) and heterogeneities
- Advantages: **non radioactive** and important available volume



*CO<sub>2</sub> gasification treatment*  
 **$T^{\circ}=950^{\circ}\text{C}$ ,  $p_{\text{CO}_2}=0.1 \text{ MPa}$ ,  $t=3\text{h}$**

**Weak relative weight loss**  
about **12 %**



Pageot et al., 2015

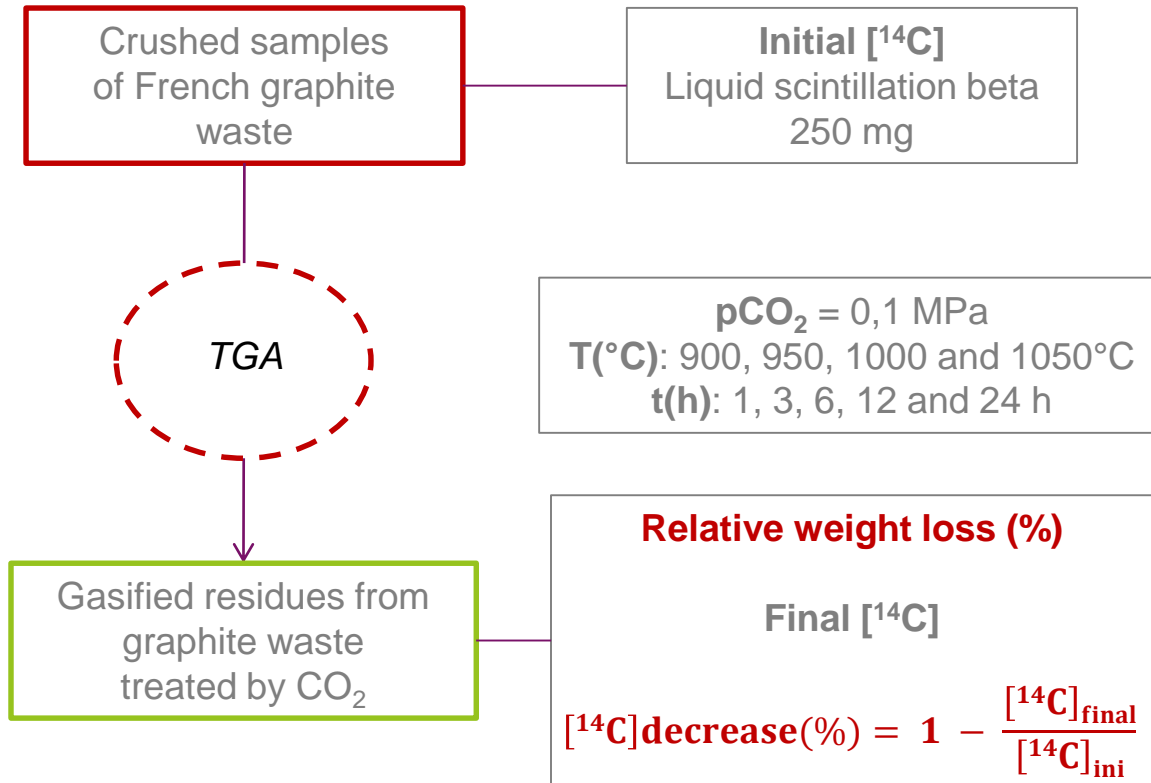
Reactivity experiments carried out at the IS2M laboratory



### Experiments on nuclear graphite waste

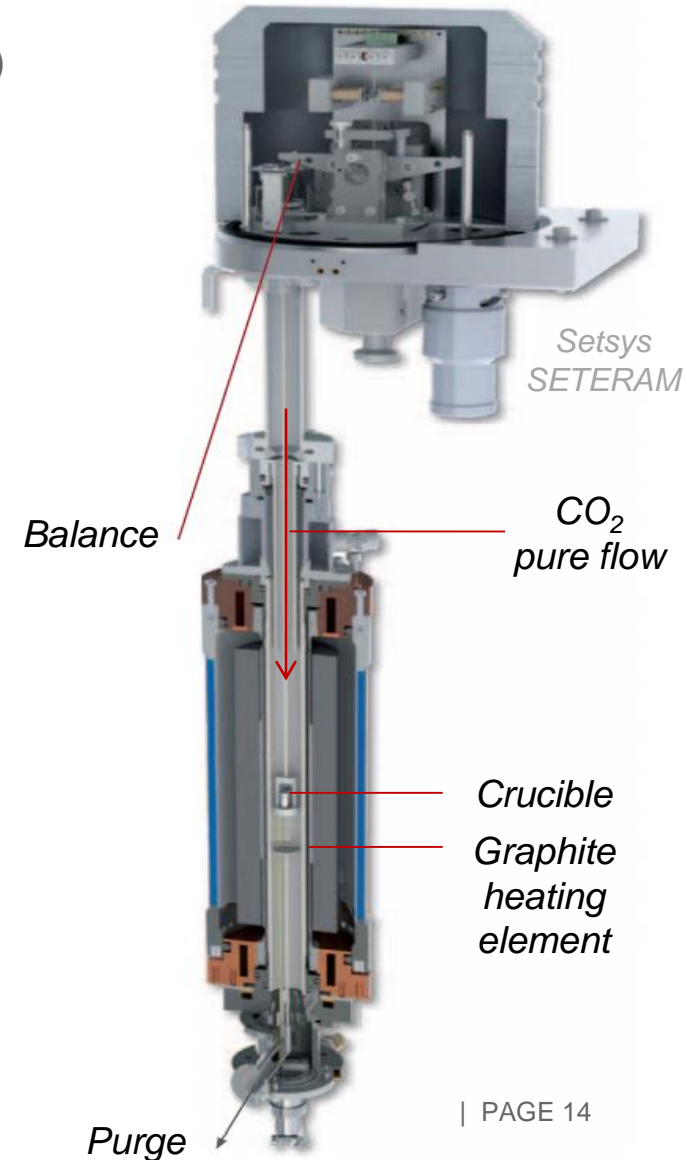
A. Duhart-Barone, S. Lutzler and J. Comte (CEA Cadarache)

Method:



Goals:

- Determine the optimal temperature in our conditions
- Gasification duration effect

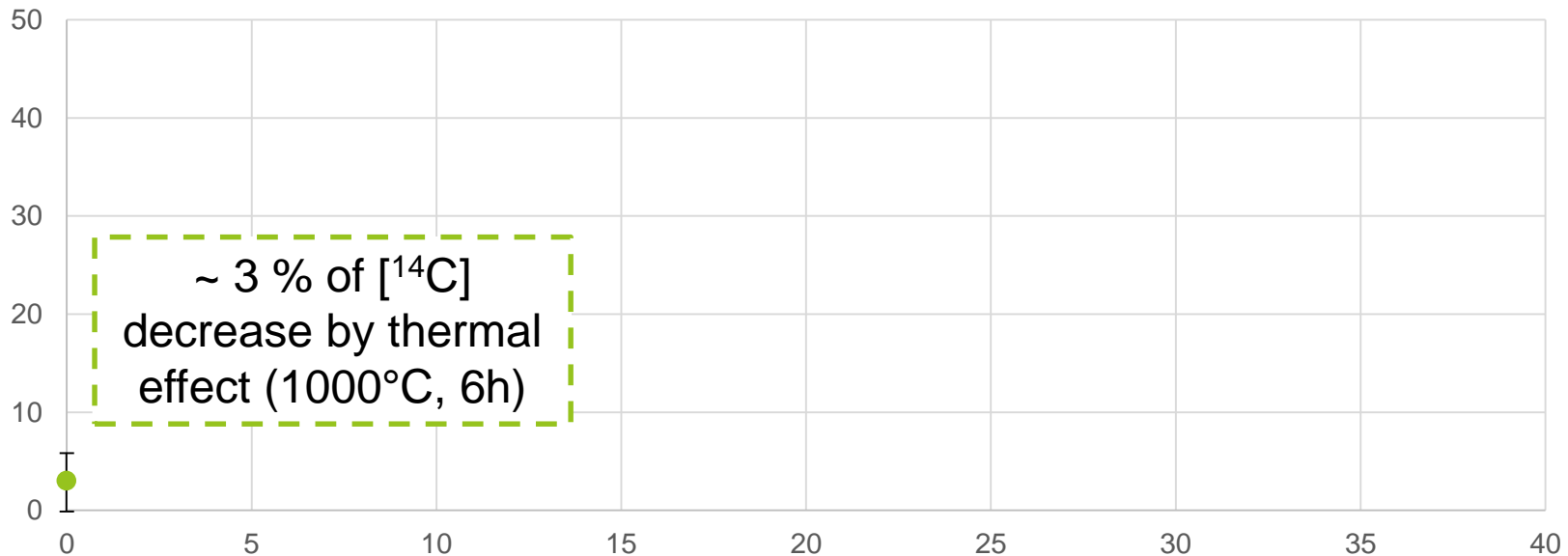


## [<sup>14</sup>C] decrease versus relative weight loss

[<sup>14</sup>C] decrease (%)

± 3%

Highly irradiated G2 sample



Relative weight loss (%) ± 0,4%

### ■ Thermal effect at 1000 °C (He)

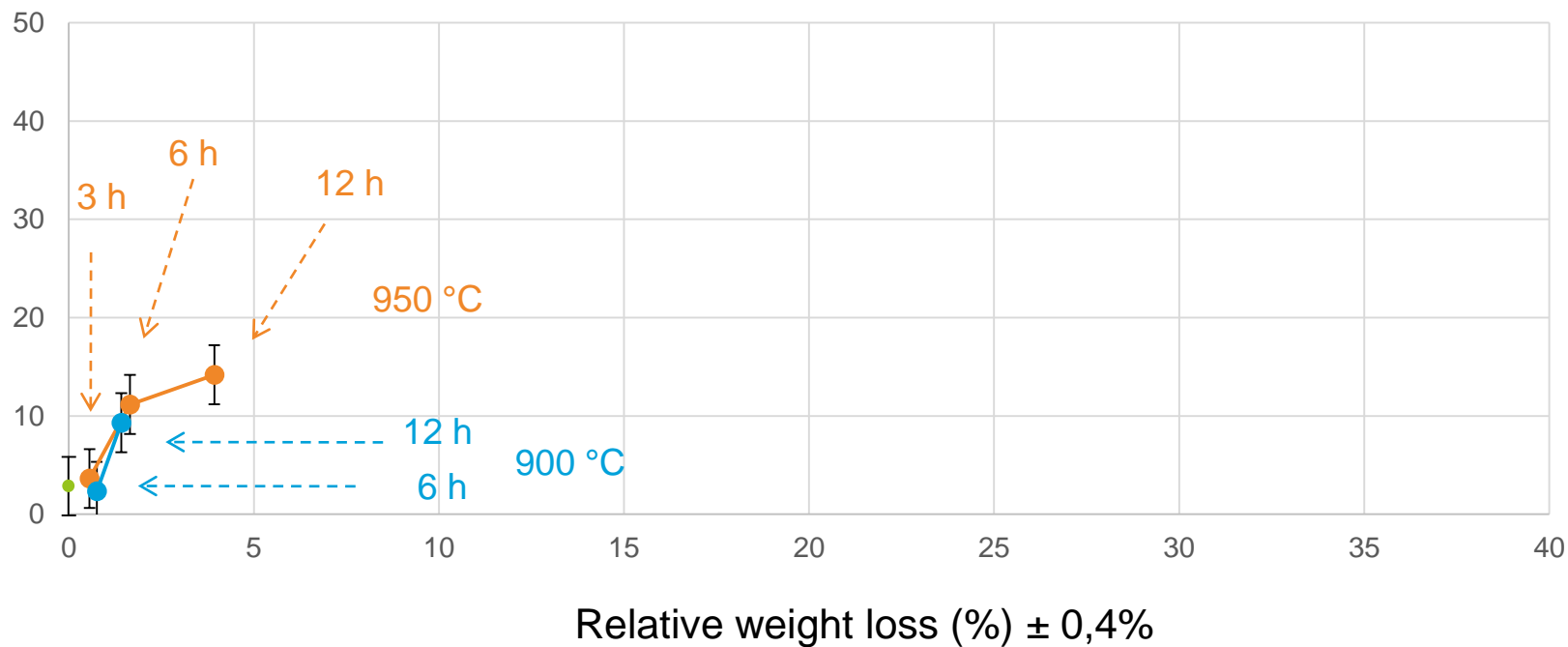
- Very weak <sup>14</sup>C extraction but measurable
- Interpretations : some of the <sup>14</sup>C is weakly linked to the graphite
- In an other sample, no thermal effect is measurable

## [<sup>14</sup>C] decrease versus relative weight loss

[<sup>14</sup>C] decrease (%)

± 3%

Highly irradiated G2 sample



### ■ T ≤ 950 °C

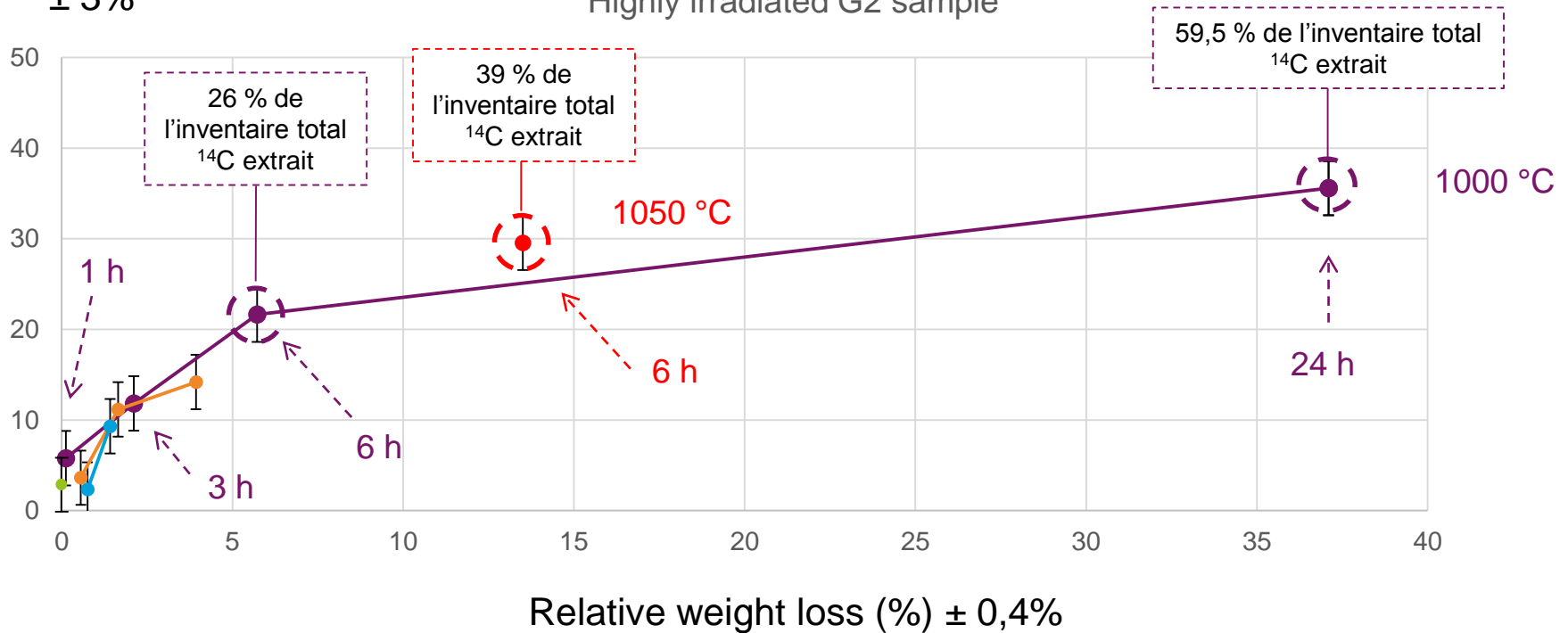
- Weak and slow reactivity.
- Weak <sup>14</sup>C extraction.
- Bad accessibility to active sites in closed and nanometer sized porosity ?

## [<sup>14</sup>C] decrease versus relative weight loss

[<sup>14</sup>C] decrease (%)

± 3%

Highly irradiated G2 sample



### ■ T ≥ 1000°C

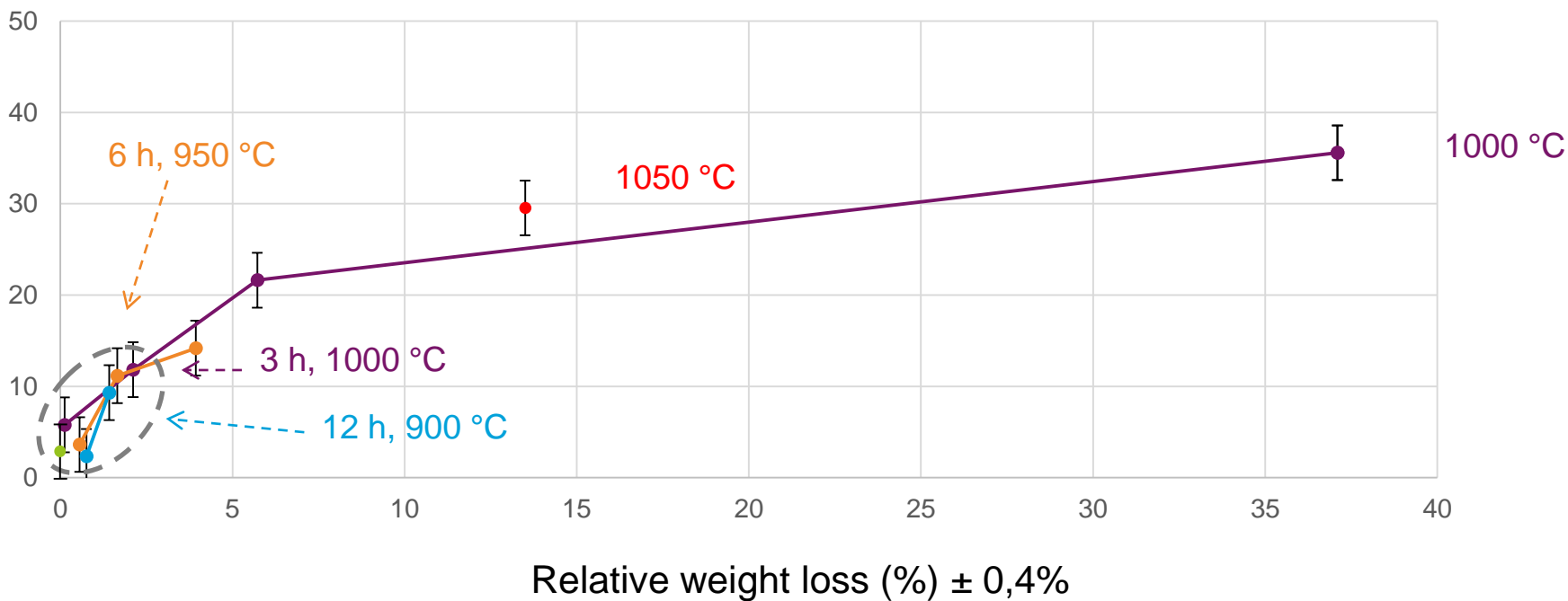
- High temperatures and long durations required
- Significant <sup>14</sup>C extraction
- Interpretations : porosity opening
- With gasification duration, selectivity decrease

## [<sup>14</sup>C] decrease versus relative weight loss

[<sup>14</sup>C] decrease (%)

± 3%

Highly irradiated G2 sample



### ■ <sup>14</sup>C extraction interpretation: 1<sup>st</sup> step (between 5 and 10% of [<sup>14</sup>C]<sub>ini</sub>)

- For the same relative weight loss, whatever the T°, <sup>14</sup>C extraction is quite the same.
- Easy <sup>14</sup>C extraction.
- By thermal effect or selectivity on the most degraded and accessible areas.

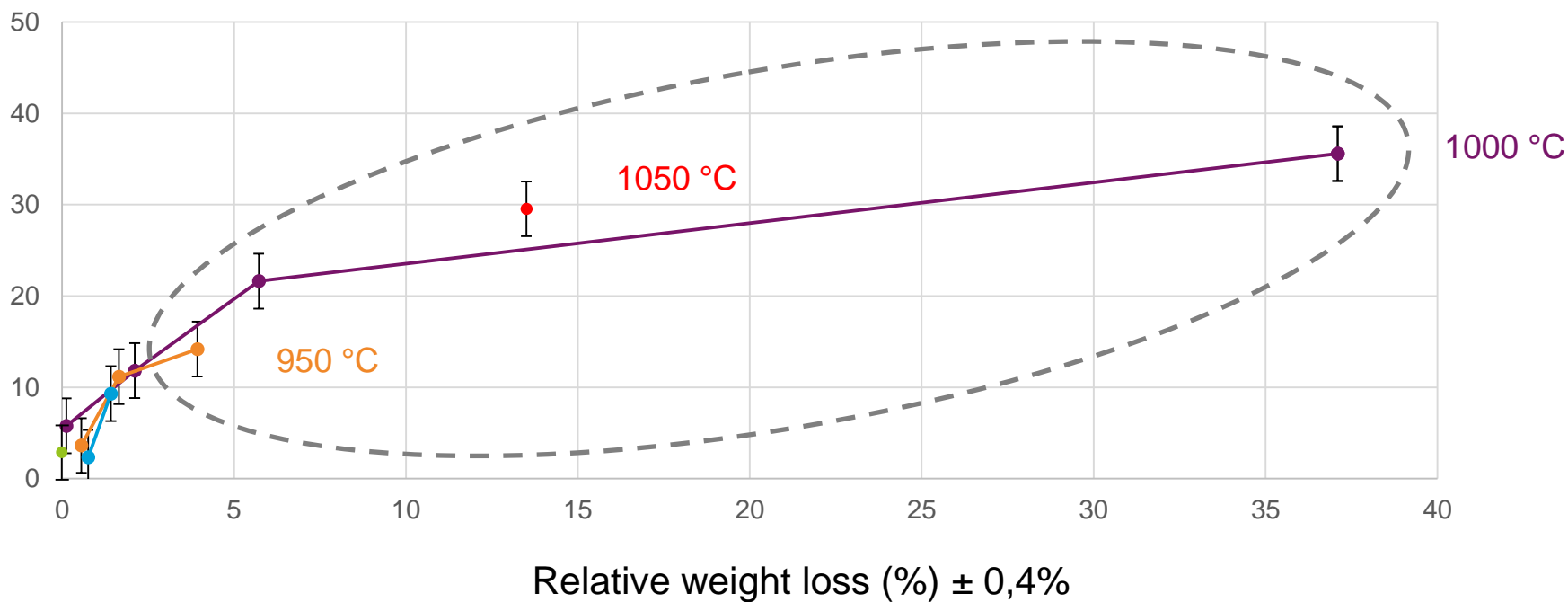


## Diminution en [<sup>14</sup>C] en fonction de la perte de masse relative

[<sup>14</sup>C] decrease (%)

± 5%

Highly irradiated G2 sample



■ <sup>14</sup>C extraction interpretation: 2<sup>nd</sup> step (remaining <sup>14</sup>C after the 1<sup>st</sup> step, 90–95% of [<sup>14</sup>C]<sub>ini</sub>)

- Dependence according to the gasification temperature.
- Extraction of <sup>14</sup>C strongly linked to graphite waste structure and hardly accessible.
- <sup>14</sup>C maybe trapped in closed porosity.
- Significant material gasification should be required.

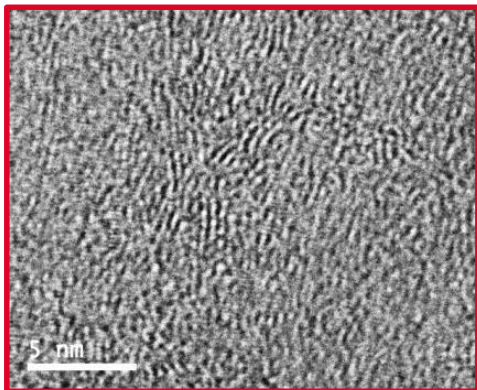
The main goal was to extract  $^{14}\text{C}$  from graphite waste

**1<sup>st</sup> step**

**2<sup>nd</sup> step**

**3<sup>rd</sup> step**

**Graphite neutron  
irradiation knowledge**



**$^{14}\text{C}$**

**Nanoporous  
nanostructure**

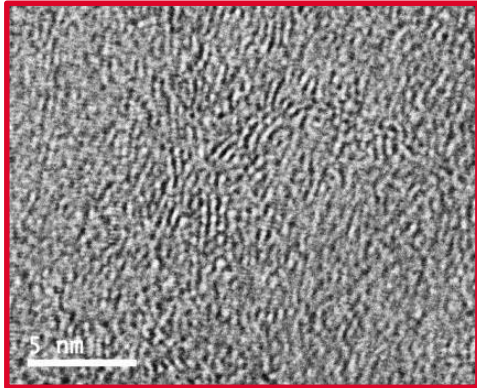
Interests of the treatment:

# CONCLUSIONS

The main goal was to extract  $^{14}\text{C}$  from graphite waste

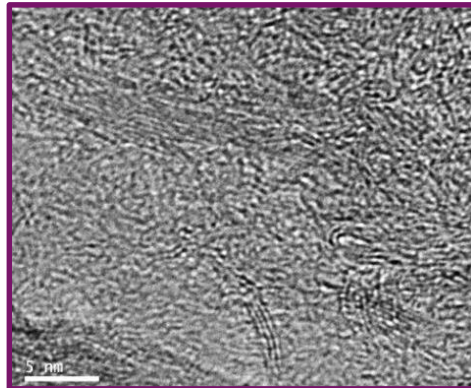
1<sup>st</sup> step

Graphite neutron irradiation knowledge



2<sup>nd</sup> step

Tests on non radioactive analogue



3<sup>rd</sup> step

$^{14}\text{C}$

Nanoporous nanostructure

Milled graphite  
Selective elimination of damaged areas starting 950°C until 1000°C

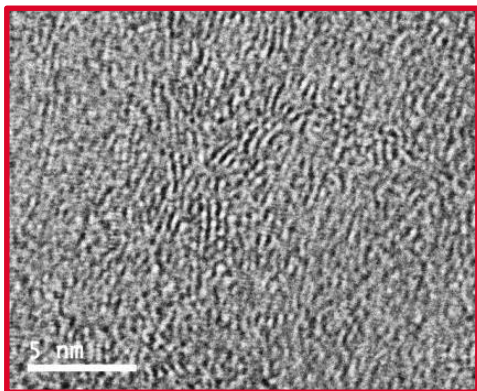
Interests of the treatment:

# CONCLUSIONS

The main goal was to extract  $^{14}\text{C}$  from graphite waste

1<sup>st</sup> step

Graphite neutron irradiation knowledge

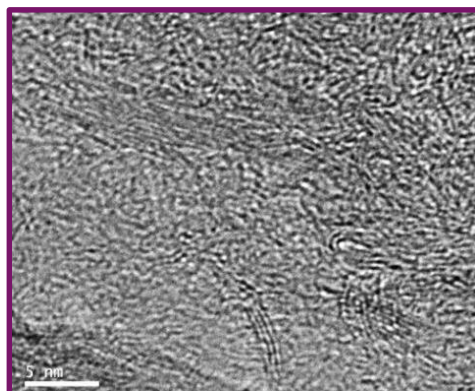


$^{14}\text{C}$

Nanoporous nanostructure

2<sup>nd</sup> step

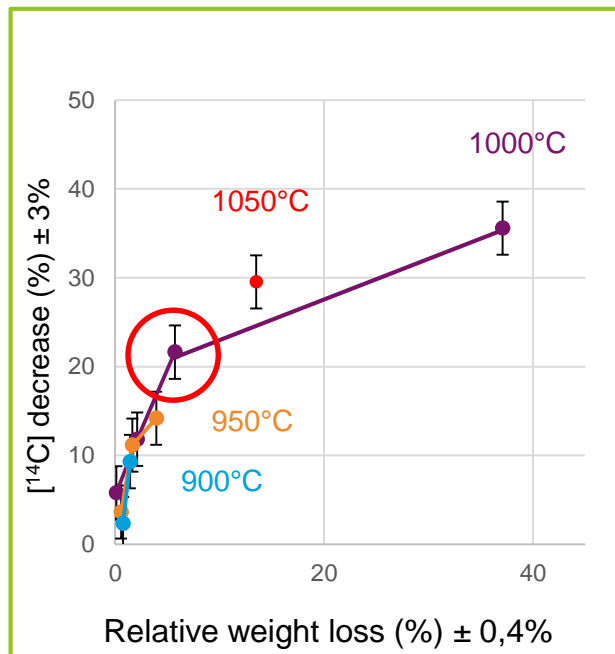
Tests on non radioactive analogue



Milled graphite  
Selective elimination of damaged areas starting 950°C until 1000°C

3<sup>rd</sup> step

Tests on nuclear graphite waste

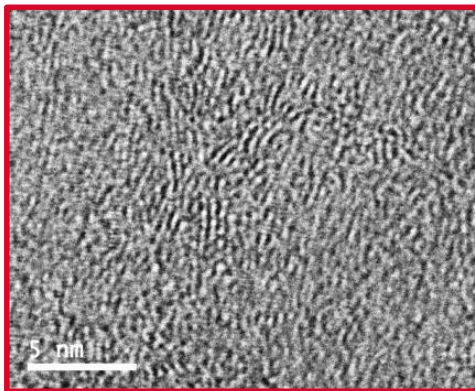


Interests of the treatment:

The main goal was to extract  $^{14}\text{C}$  from graphite waste

1<sup>st</sup> step

Graphite neutron irradiation knowledge

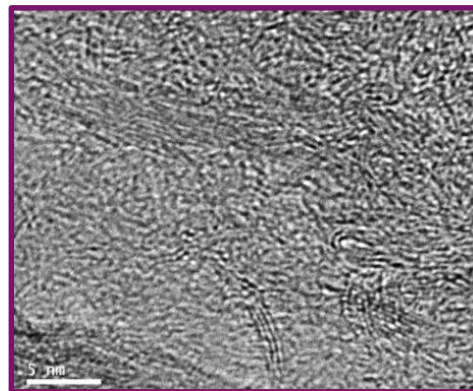


$^{14}\text{C}$

Nanoporous nanostructure

2<sup>nd</sup> step

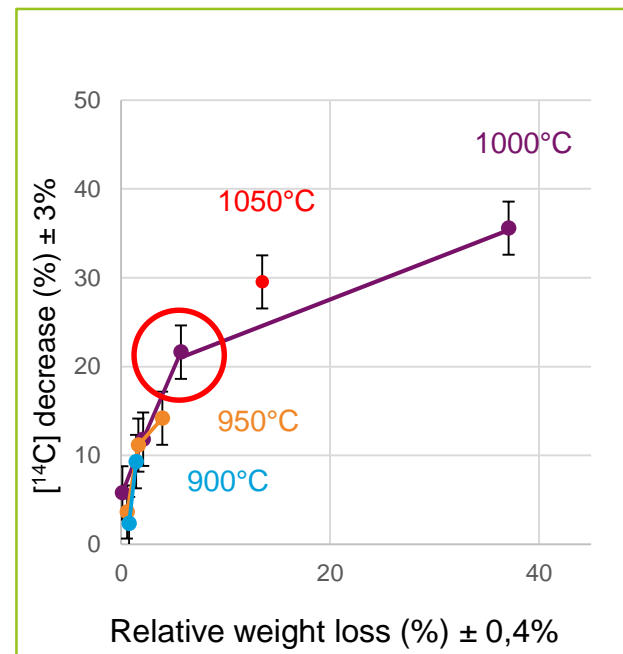
Tests on non radioactive analogue



Milled graphite  
Selective elimination of damaged areas starting 950°C until 1000°C

3<sup>rd</sup> step

Tests on nuclear graphite waste



Interests of the treatment:

- To decrease the activity
- To extract the most « mobile »  $^{14}\text{C}$
- The treatment process is easily optimizable



## Acknowledgments



- Andra: Laurence PETIT, Stéphane CATHERIN, financial support
- EDF R&D: Laurent PETIT, financial support
- CEA/LPCMI: Lionel GOSMAIN, Lionel SEJOURNE, Patrick BOTTIN
- CEA/LM2E: Catherine DESSEROUER, Bénédicte VERHAEGHE
- CNRS/LG-ENS: Jean-Noël ROUZAUD, Damien DELDICQUE
- CEA/LG-ENS: Emeline CHARON
- CNRS/IS2M: Mouhamad ALI AHMAD, Joseph DENTZER, Roger GADIOU
- CEA/LARC: Jérôme COMTE and his colleagues
- CEA/LECD: Anne DUHART-BARONE, Sylvie LUTZLER, Dominique CARRE
- CEA/SEMI: employees and students
- Université Paris 11/ED MIPEGE



Thank you for your attention  
Questions ?