Ion irradiation used as surrogate for neutron irradiation to understand nuclear graphite evolution during reactor operation: consequences for the long lived radionuclide's behavior

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Issues for the management of irradiated graphite waste

- Worldwide ~ 250,000 tons irradiated graphite waste (most moderators or reflectors of CO_2 cooled reactors)

- LL-LLW waste: main management solution : disposal (with or without prior purification)

- Long lived non sorbing dose determining radionuclides likely to be released out of the disposal

^{14}C : $T_{1/2} \sim 5730$ years → Release under organic (anionic) form

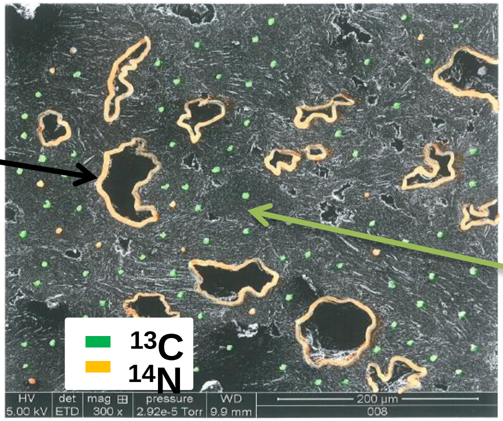
^{36}Cl : $T_{1/2} \sim 300\,000$ years → Release due to the mobility of Cl^- in clay host rocks

→ Gain information on inventory, speciation and location in nuclear graphite after reactor shutdown

What we already know on ^{14}C and ^{36}Cl in nuclear graphite

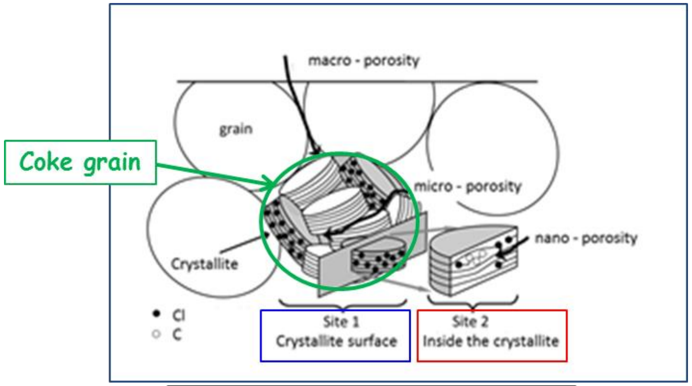
^{14}C : two different origins inducing contrasted locations

^{14}C issued from ^{14}N
$^{14}N(n,p)^{14}C$
(mainly close to pores ^{14}N is adsorbed during maintenance cycles)
released by radiolytic corrosion
(in CO_2 cooled reactors)



^{14}C issued from ^{13}C
$^{13}C(n,\gamma)^{14}C$
(mainly in the bulk)
stable up to T ~ 1600°C

^{36}Cl : mainly produced through the activation of ^{35}Cl (nuclear graphite impurity) $^{35}Cl(n,\gamma)^{36}Cl$



Chlorine is covalently bound to carbon

^{36}Cl release related to the structure of graphite

↓

^{36}Cl located at crystallite edges released from T = 200°C

^{36}Cl located inside crystallites released at T > 1200°C

G. Silbermann et al. Nuclear Instruments and Methods in Physics Research Section B 332 (2014) 106 -110
N. Moncoffre et al. Journal of Nuclear Materials 472 (2016) 252-258

C.E. Vaudey et al. Journal of Nuclear Materials 395 (2009) 62-68
C.E. Vaudey et al. Journal of Nuclear Materials 418 (2011) 16–21
A. Blondel et al. Carbon 73 (2014) 413-420
N. Toulhoat et al. Journal of Nuclear Materials 464 (2015) 405–410

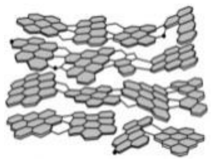
Question : Behavior of ^{14}C and ^{36}Cl during reactor operation?

Impact of neutron irradiation + temperature on the ^{14}C and ^{36}Cl behavior?

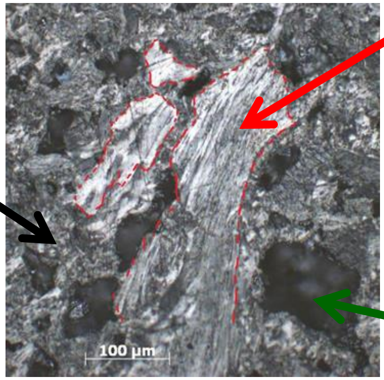
- ✓ **How does irradiation modify the graphite structure**
- ✓ **How does the structure modification influence the radionuclides release?**

^{37}Cl or ^{13}C implantation to simulate ^{36}Cl or ^{14}C

Binder (made of coal tar pitch)



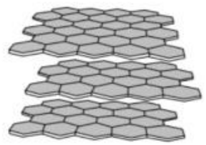
Less ordered



Nuclear graphite

Pore

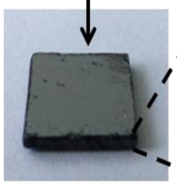
Filler (Coke grain) ~ 80%



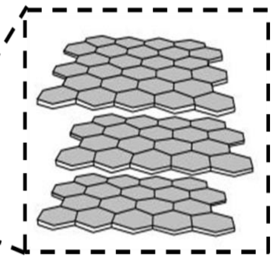
Well ordered

Highly Ordered Pyrolytic Graphite HOPG to simulate coke grains

Implantation

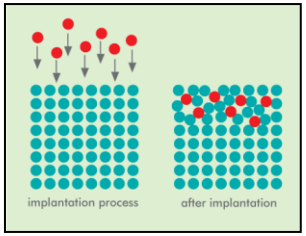


HOPG sample



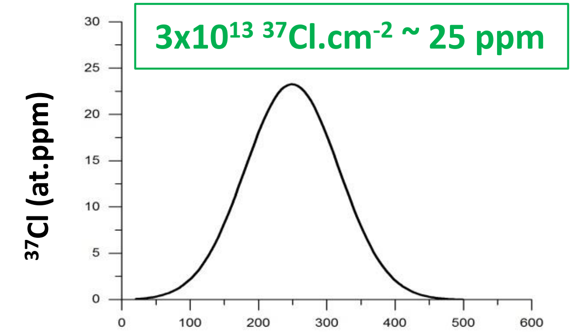
HOPG model graphite

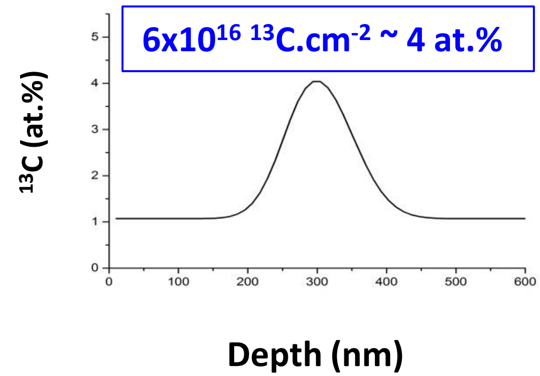
Ion implantation



^{37}Cl

^{13}C



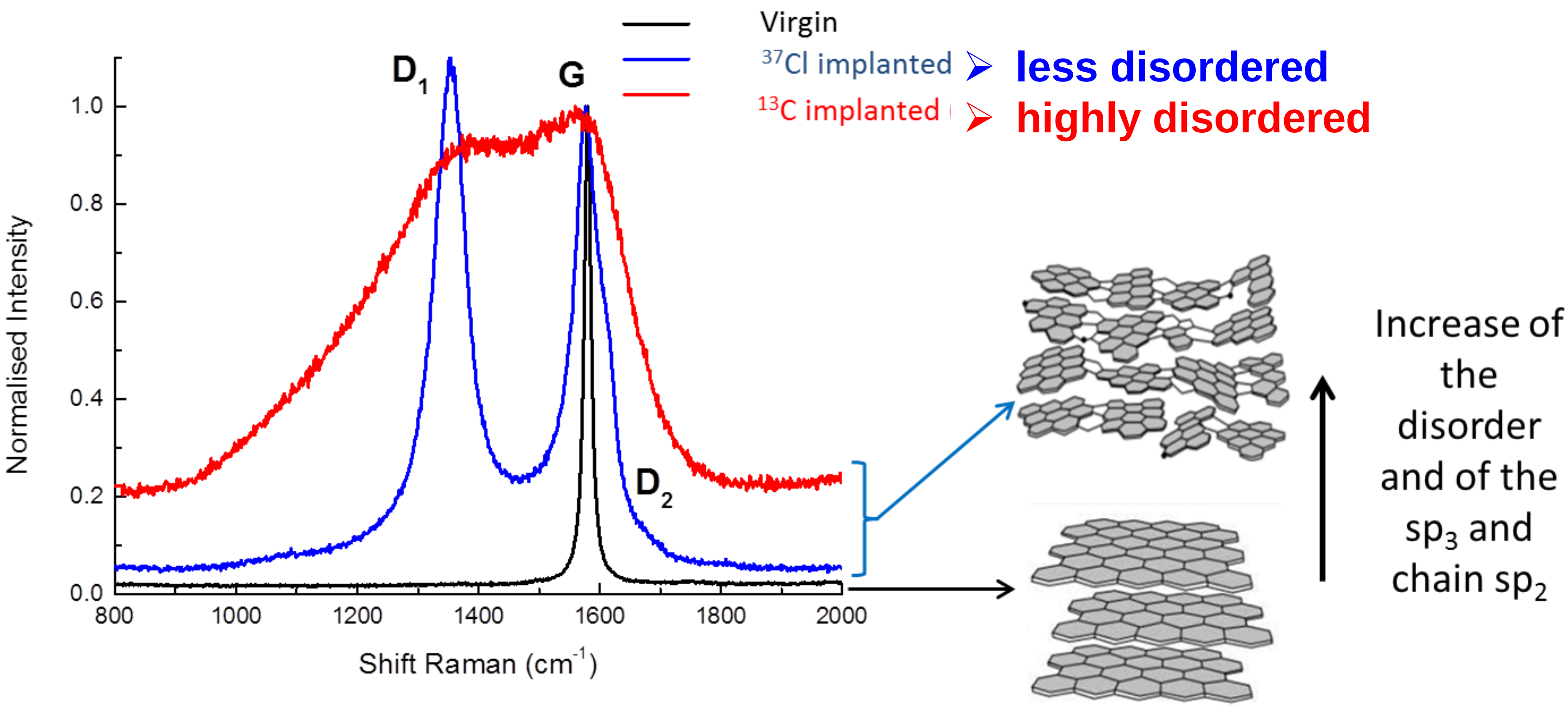


Depth (nm)

^{37}Cl or ^{13}C implantation to simulate ^{36}Cl or ^{14}C
(measured by SIMS)

Two different structural states

Implantation alows simulating two different structural states :



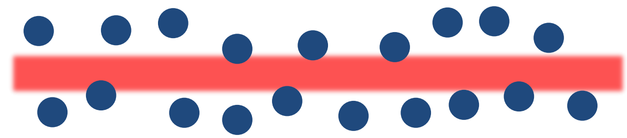
G mode : planar vibrations of C atoms
D mode : hetero-atoms, vacancies, grain boundaries and other defects

I_{D1}/I_G and $FWHM_G$ parameters : monitor the graphite structure disorder

Ion irradiation to simulate neutrons

Neutrons generate atom displacements producing mainly Ballistic damage (1 - 3 dpa)

Recoil carbon atoms transfer some energy through excitations and ionisations



Stopping power (S_{tot}) =

Nuclear stopping power ($\mathbf{S_n}$) + Electronic stopping power ($\mathbf{S_e}$)

Ions used to simulate neutron irradiation effects

	Energy (MeV)	Se (keV/µm)	dpa
Carbon	0.4 – 0.6	585 - 730	1
Argon	0.8	980	4
Helium	15.7	75	0.0001
Sulfur	100	3700	0.002
Iodine	200	16700	0.04

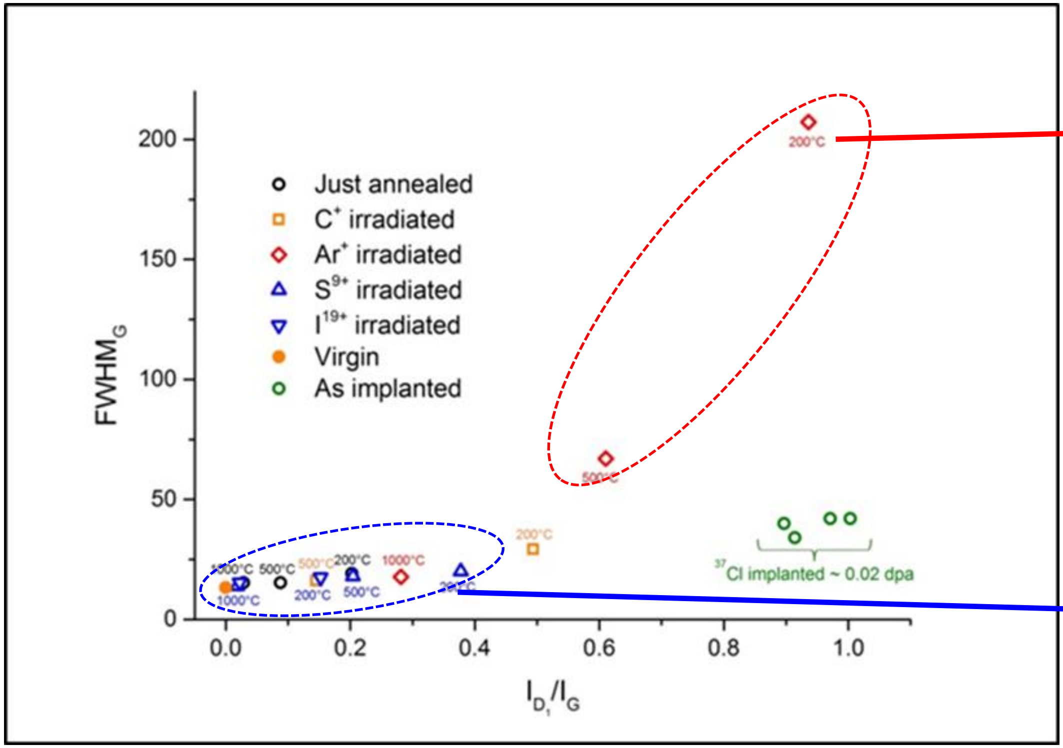
Ballistic regime is favored (Carbon, Argon)

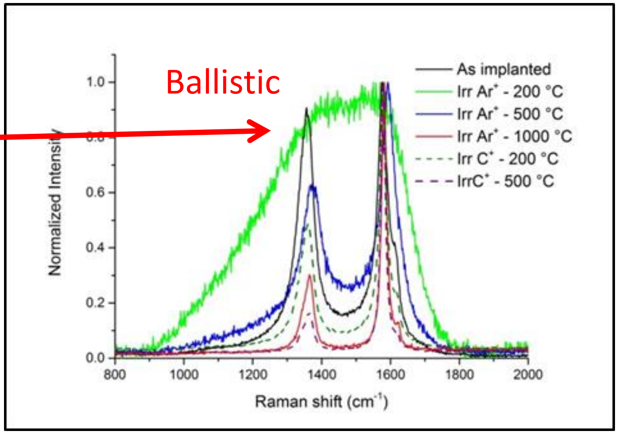
Electronic regime is favored (Helium, Sulfur, Iodine)

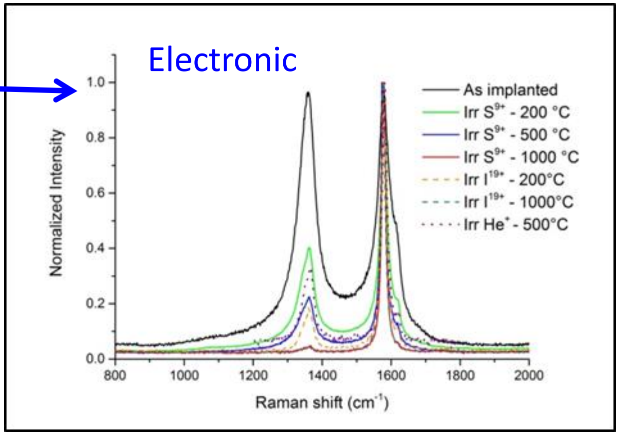
Structure evolution

Less disordered structure through implantation

3D reordering







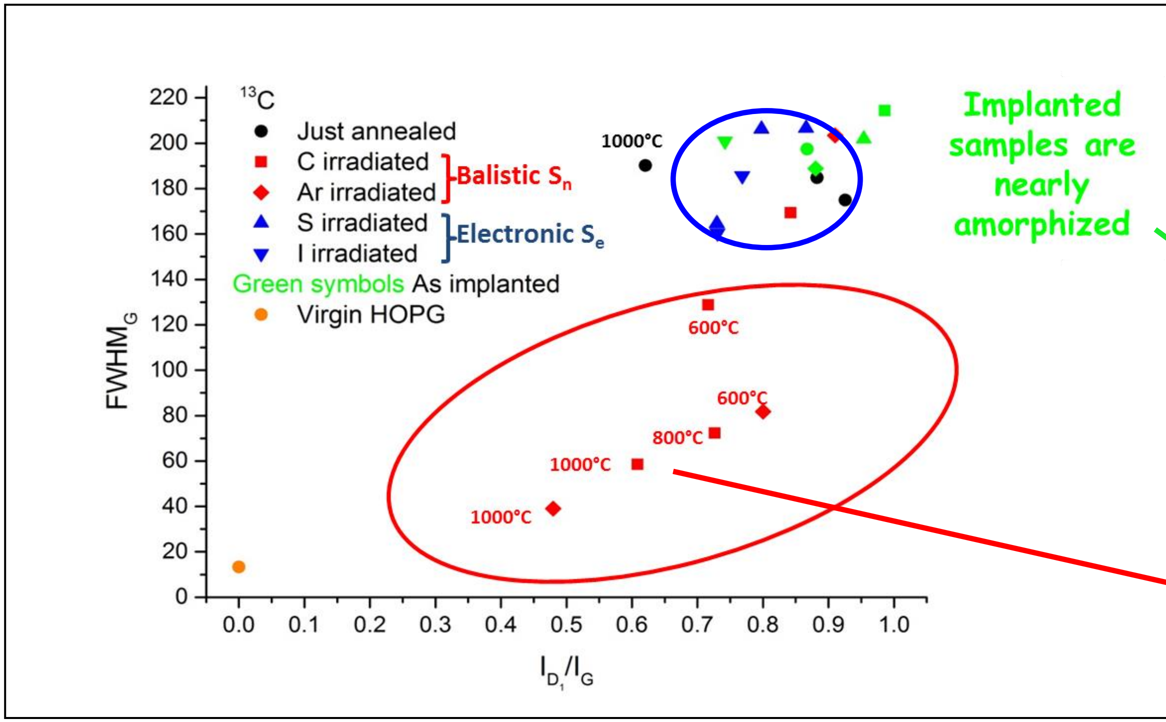
In plane reordering

- Ballistic irradiation (dpa >> 1) : **strong disordering** compensated by temperature annealing effects

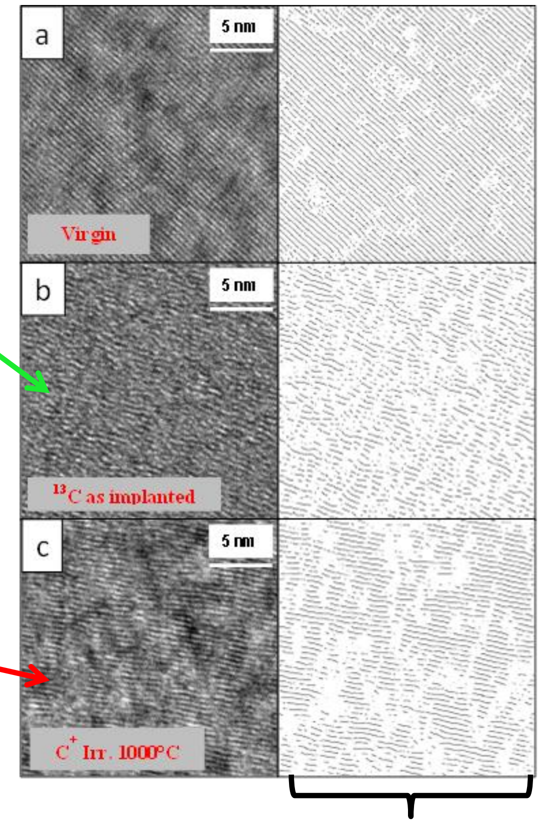
- Electronic regime or ballistic at low dpa level : almost no impact on disordering

Structure evolution

Highly disordered structure through implantation



HRTEM and squeletonized images

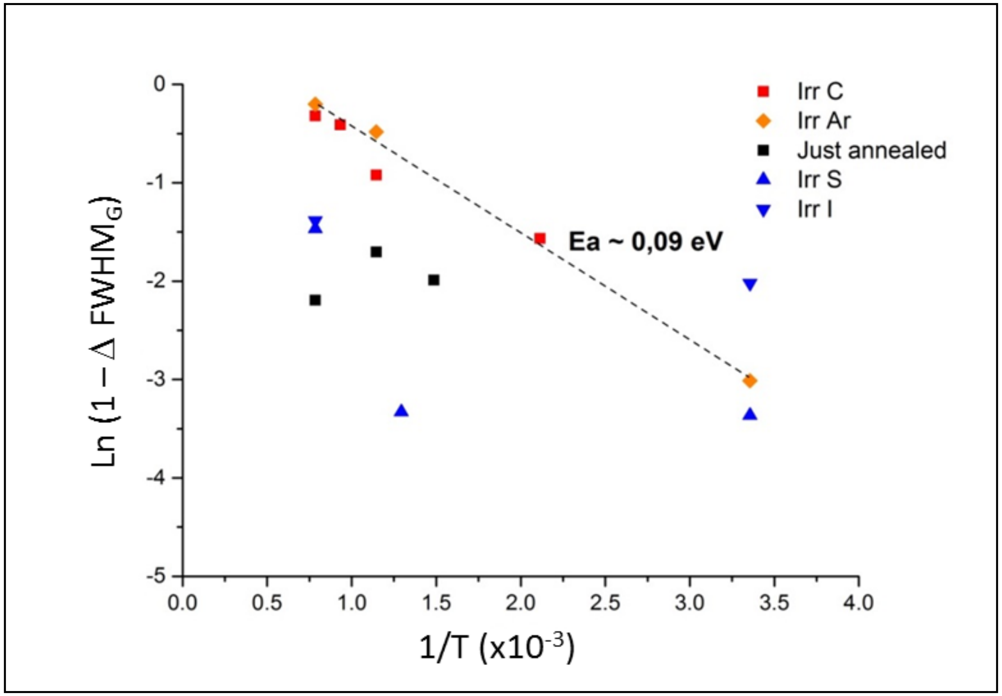


Increase of the size of the coherent domains

- Temperature alone or electronic regime : no impact
- **Ballistic irradiation + temperature : three dimensional reordering of the structure**

Reordering process

Highly disordered structure through implantation



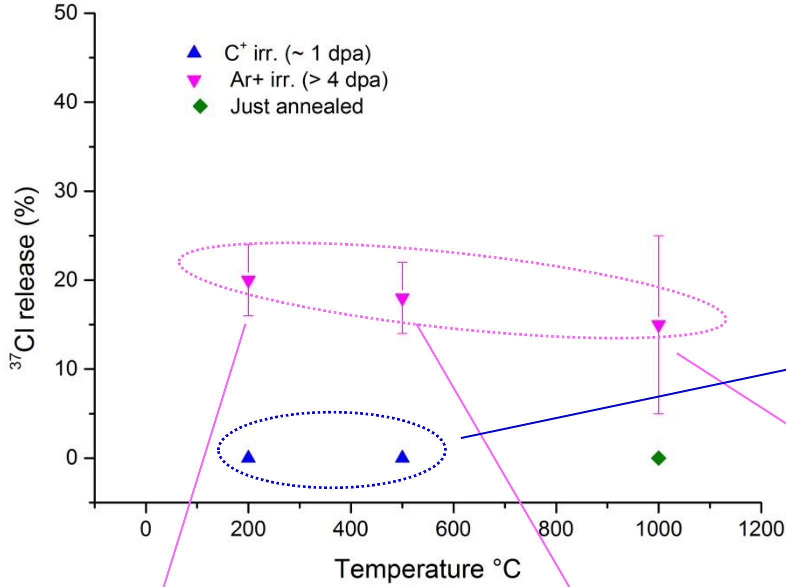
$$\Delta \text{ FWHM} = \frac{\text{FWHM irradiated}}{\text{FWHM unirradiated}}$$

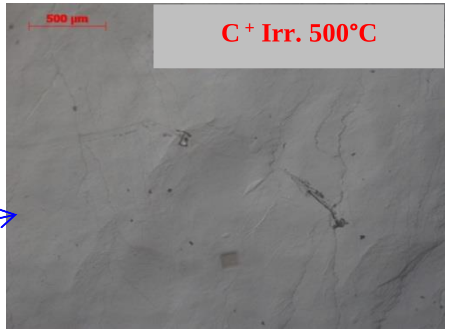
Ea ~ 0.09 eV

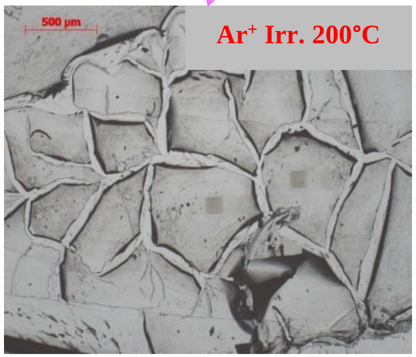
Higher Ea values reported in the literature to achieve three dimensional temperature reordering

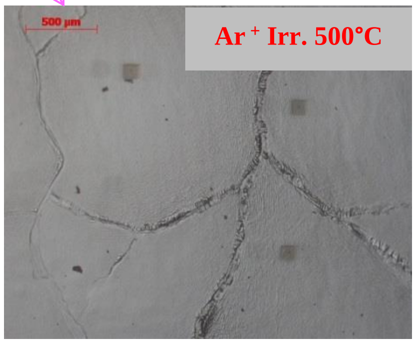
Very low reordering activation energy → Athermal radiation enhanced annealing process (break-up of clusters and vacancy-interstitial annihilation)

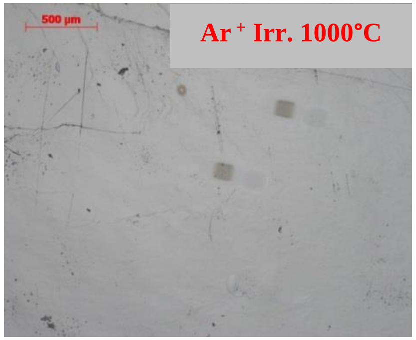
^{37}Cl release under irradiation

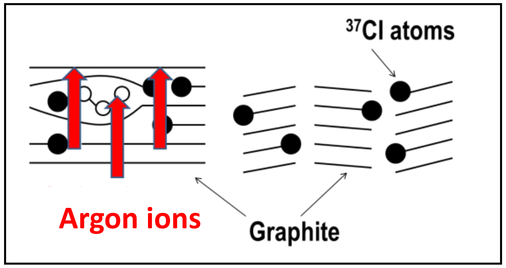










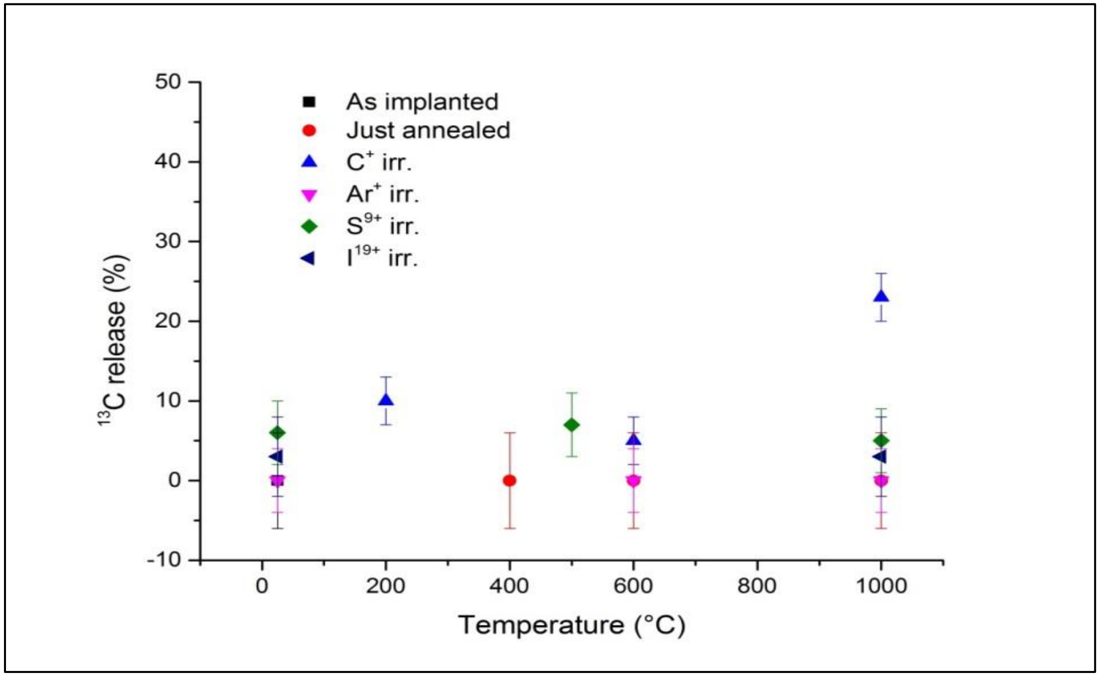


Argon irradiation (dpa >> 1) break the graphene planes

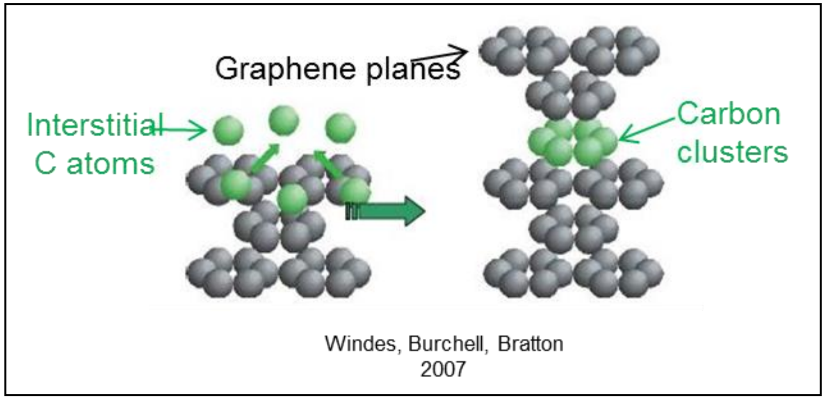
⬇

^{37}Cl at broken crystallite edges is released

^{13}C release under irradiation



Almost no ^{13}C release whatever the irradiation conditions



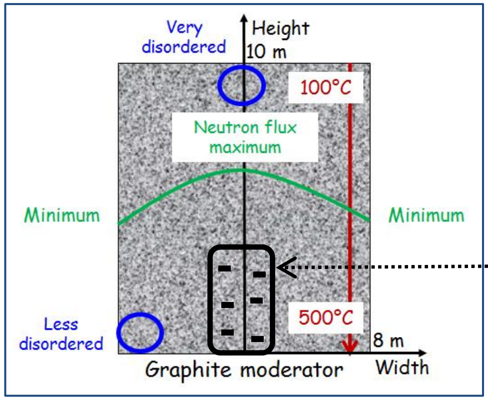
^{13}C might be stabilized into new formed carbon clusters?

Inferred behavior for ^{14}C and ^{36}Cl in irradiated graphite

Irradiation (ballistic damage) + Temperature

- Favor ^{14}C incorporation into new carbon structures
- Favor ^{36}Cl release (more than 30% released in hot and highly irradiated areas)

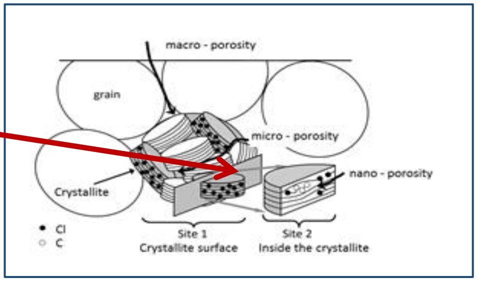
Nature and initial structural state (binder, coke), irradiation history and position of graphite in the reactor will lead to significant structural heteroneneities



Depleted ^{36}Cl zones

High temperature annealing (T > 1300°C) prior to disposal should in any case be beneficial

- To stabilize ^{14}C
- To release ^{36}Cl bound to edge planes (which should be more accessible to leaching)



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Thank you for your attention !