Current status of materials and K-factor results in the IRENE project

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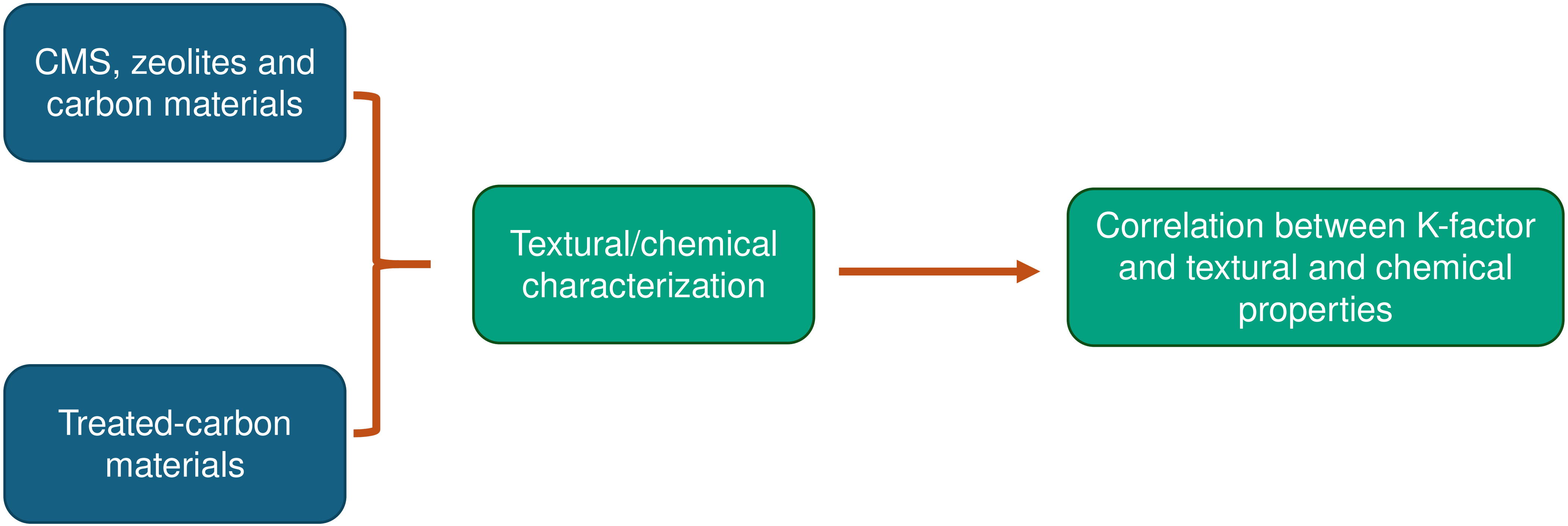
Materials: synthesis and characterization

- Tannin-derived carbons: DMC and OMC
- C12-derivatives, zeolites and CMS
- N-doped graphitic carbons
- Ag-carbon composites

Multi-gas adsorption and K-factor

Conclusions and next steps

General characterization workflow



Selected samples were submitted to **additional** noble gas adsorption **measurements**: Ar, Kr and Xe

Synthesis of DMC and OMC from mimosa tannin

DMC → Disordered mesoporous carbon
OMC → Ordered mesoporous carbon

Common precursor system

- **T** Mimosa tannin
- **P** Pluronic® F127 (PEO–PPO–PEO)
- **W** Distilled water

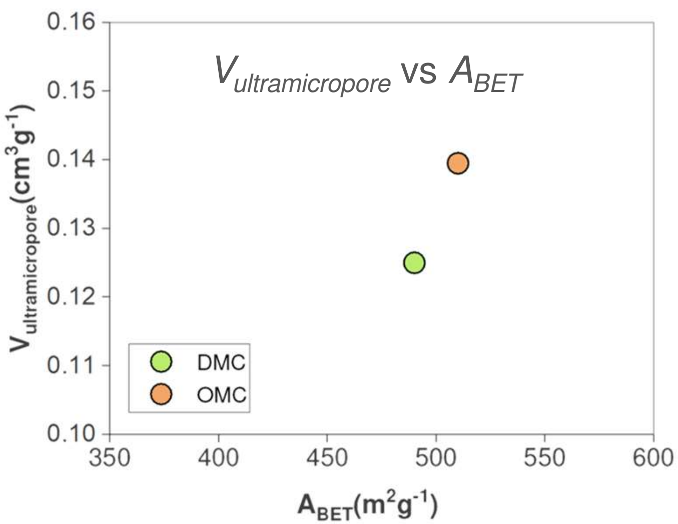
T:P:W = 2:2:2 g → **DMC**

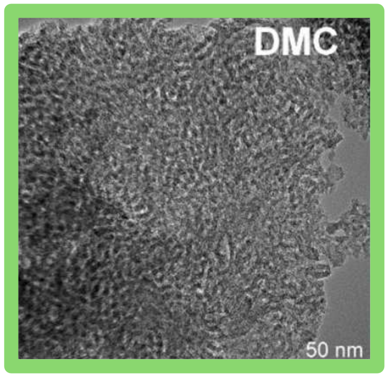
T:P:W = 2:0.75:1.75 g → **OMC**

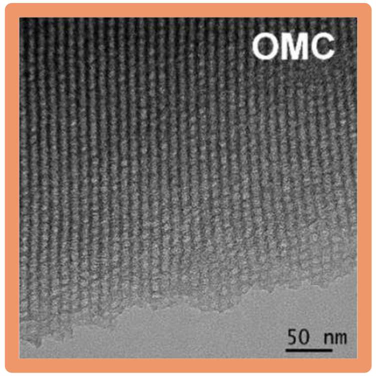
Ball milling, 1 h

Carbonization, 900 °C, 1 h, N_2

SAMPLE	CODE
DMC-Ball Milling	DMC*
OMC-Ball Milling	OMC*







TEM images adapted from Castro-Gutiérrez, J. (2020)

* 2 samples → iSm2 lab

Materials

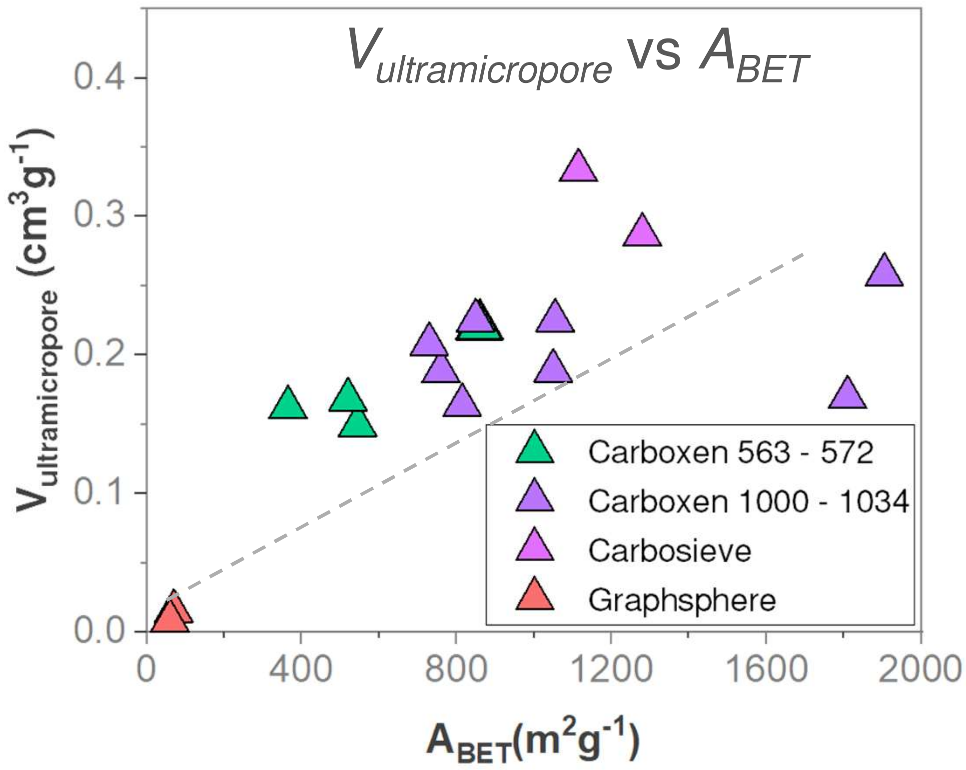
Group	Definition	Number of samples	Samples with K-factor data	Textural analysis	EA
CMS	Carbon molecular sieves	16	3	16	-
Zeolites	Zeolites (pristine and Ag-exchanged)	5	2	5	-
Carbons	Commercial carbon materials and treated carbons	22	11	22	19

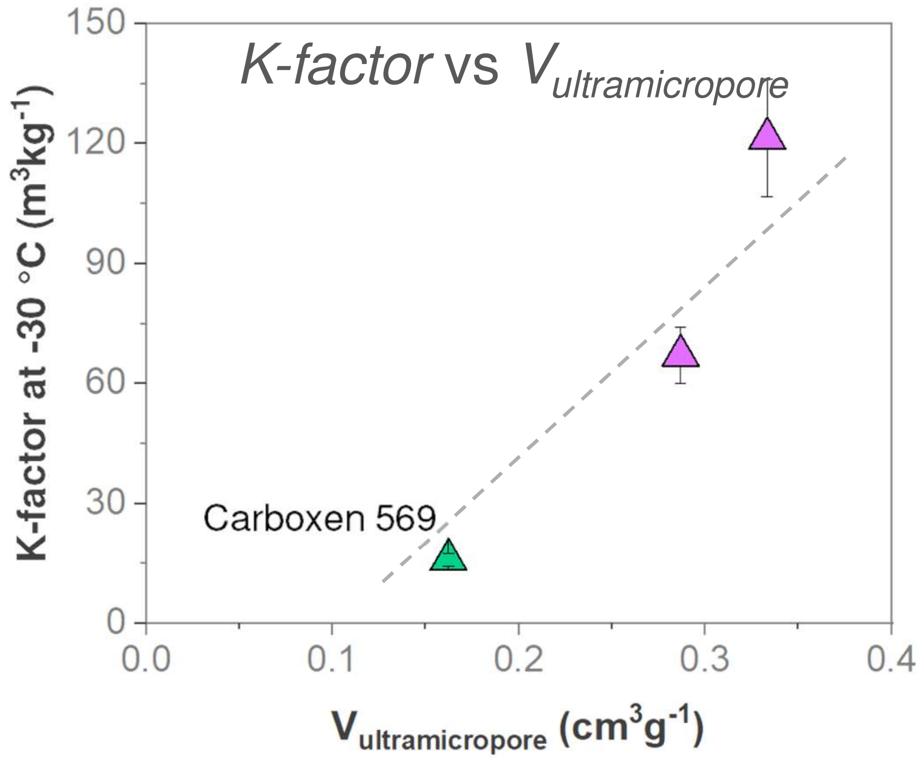
K-factor data were collected at **different temperatures**, depending on the material

This work aims to identify which textural and chemical parameters control the K-factor

Many materials were **prepared** and more than **40 characterized**

CMS are porous carbons with **narrowly** distributed micropores for **selective gas separation**



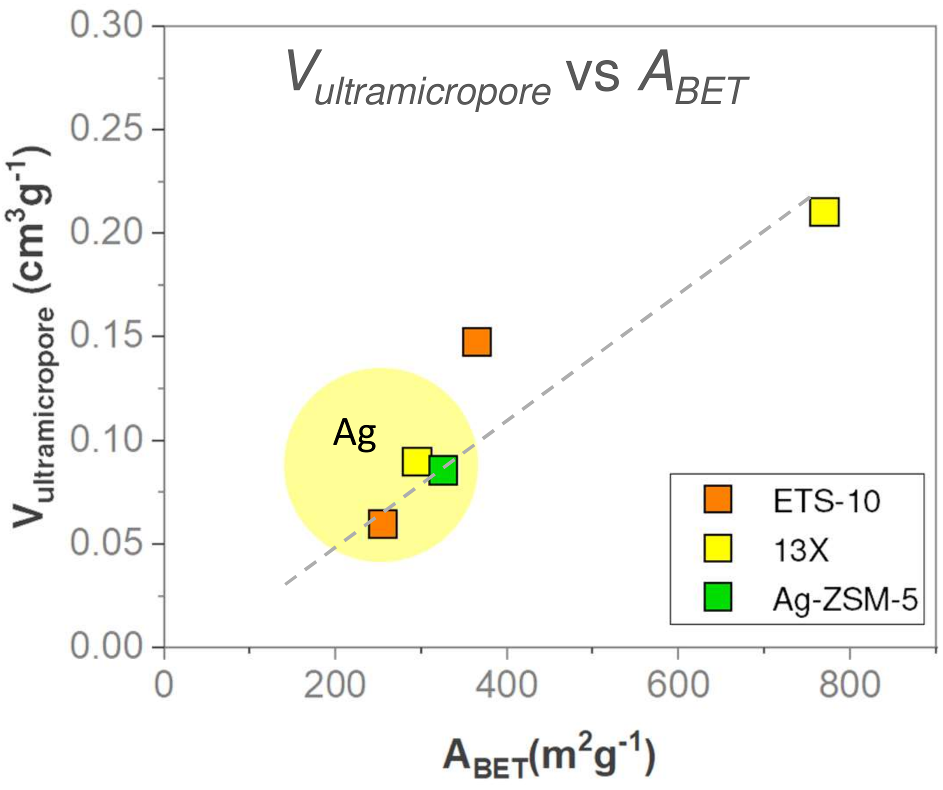


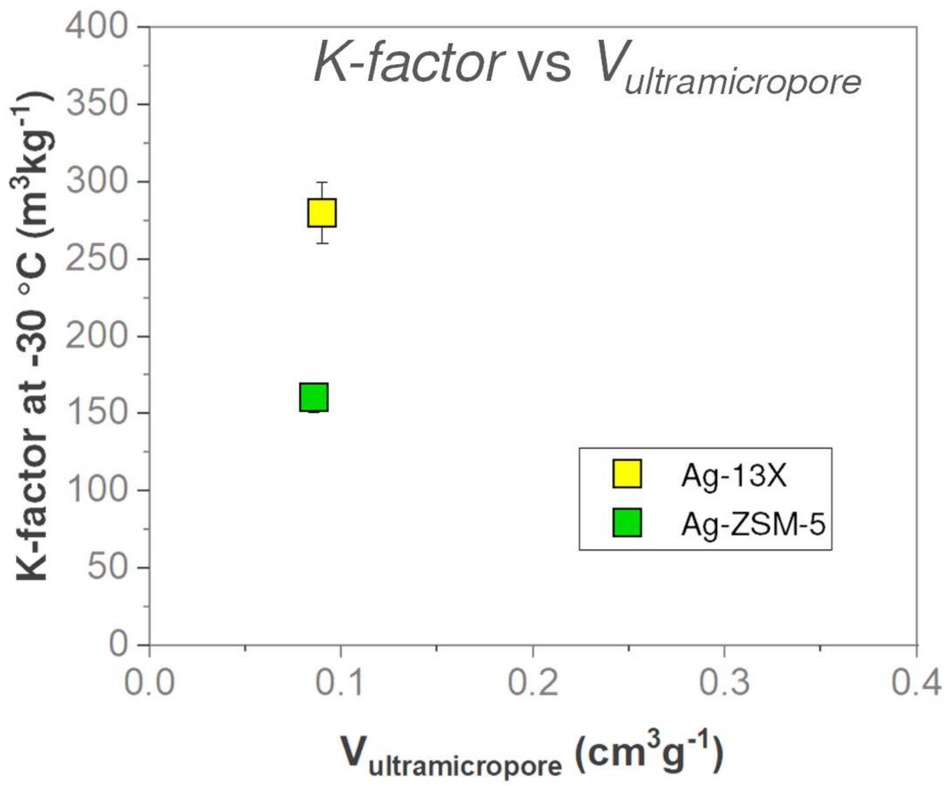
CMS exhibit a broad range of $\mathbf{A_{BET}}$ and $\mathbf{V_{<0,7nm}}$

Under these conditions, **K-factor** is associated with $\mathbf{V_{<0,7nm}}$

Data are **shown at -30 °C**, where the largest dataset is **available**

Zeolites: textural properties and K-factor

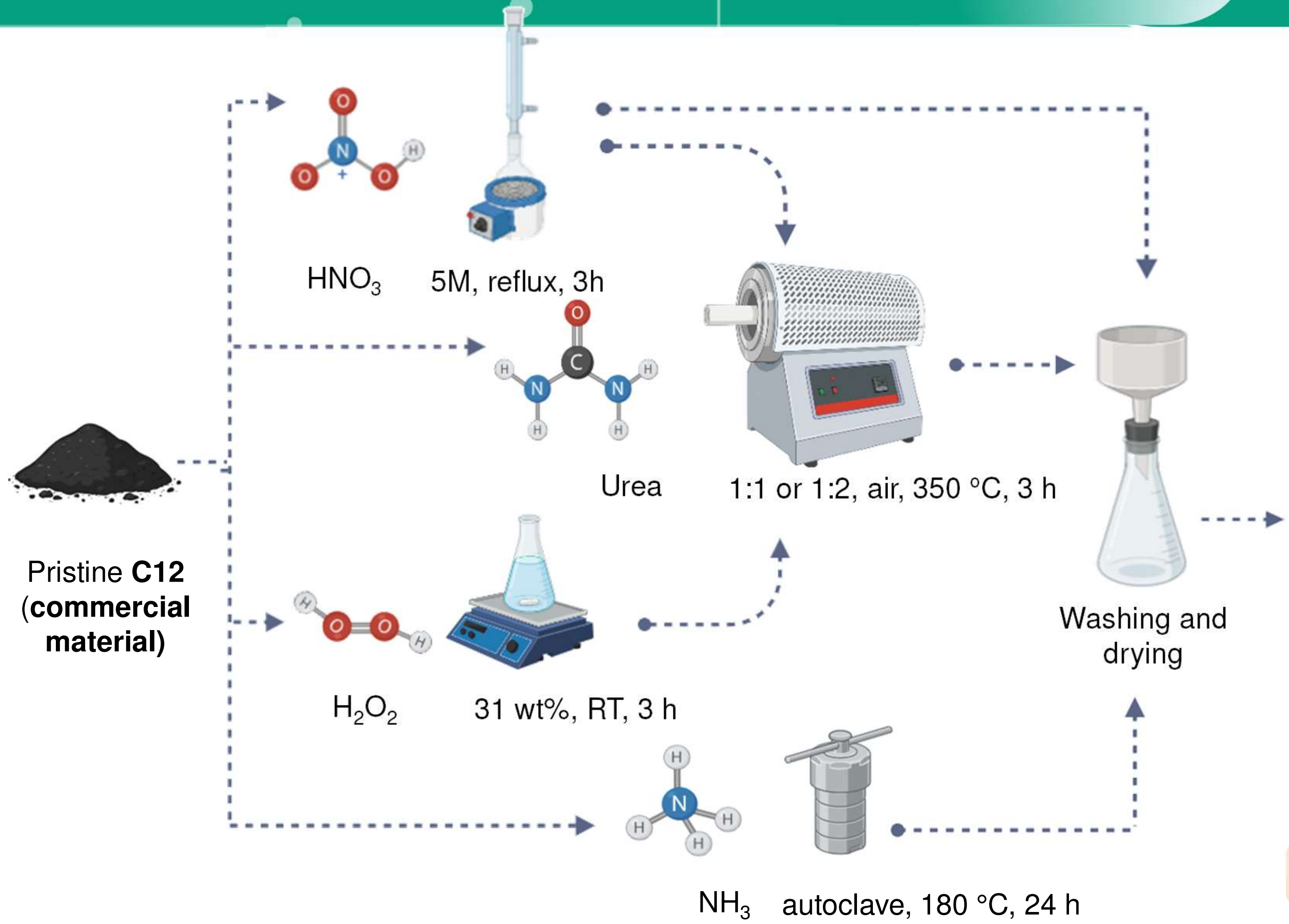




Ag-containing zeolites are highlighted in yellow

The **K-factor plot** includes only **two data points**

Preparation route for C12-based carbons



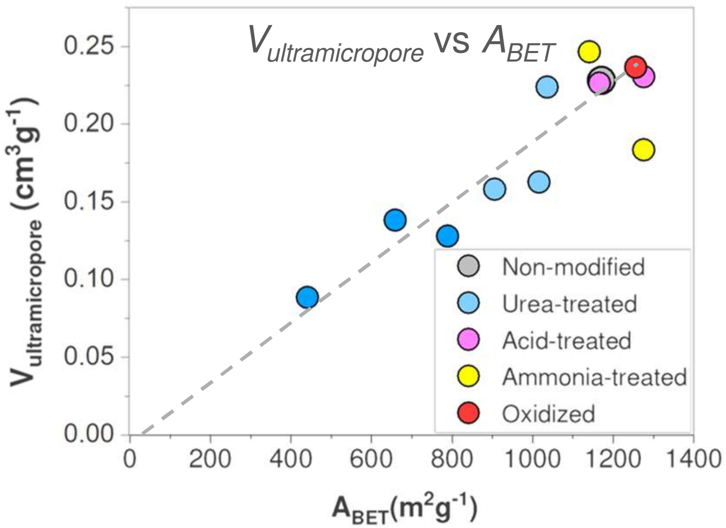
SAMPLE	CODE
Pristine C12	C12
C12/UREA 1:1	U1*
C12/H_2O_2/UREA 1:1	O-U1*
C12/HNO_3/UREA 1:1	HNO_3-U1*
C12/UREA 1:2	U2*
C12/HNO_3/UREA 1:2	HNO_3-U2*
C12/H_2O_2/UREA 1:2	O-U2*
C12/HNO_3	HNO_3*
C12/H_2O_2/HNO_3	O-HNO_3*
C12/NH_3	NH_3*
C12/H_2O_2/NH3	O-NH_3*
C12/H_2O_2	O

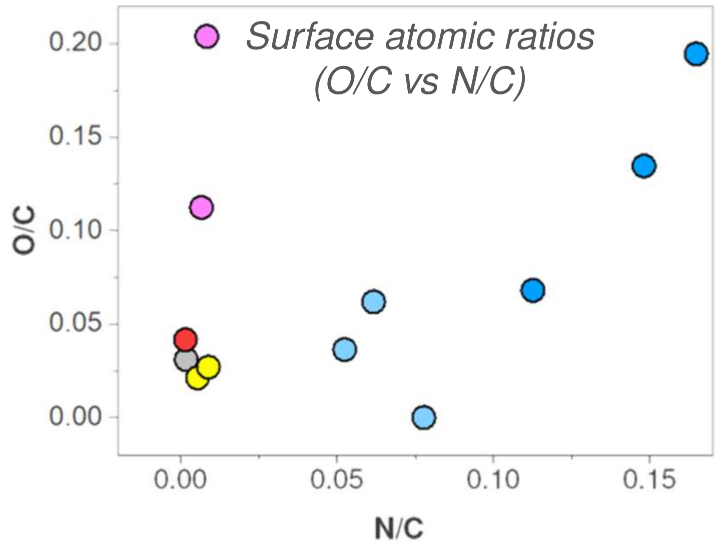
*10 samples → CPPM

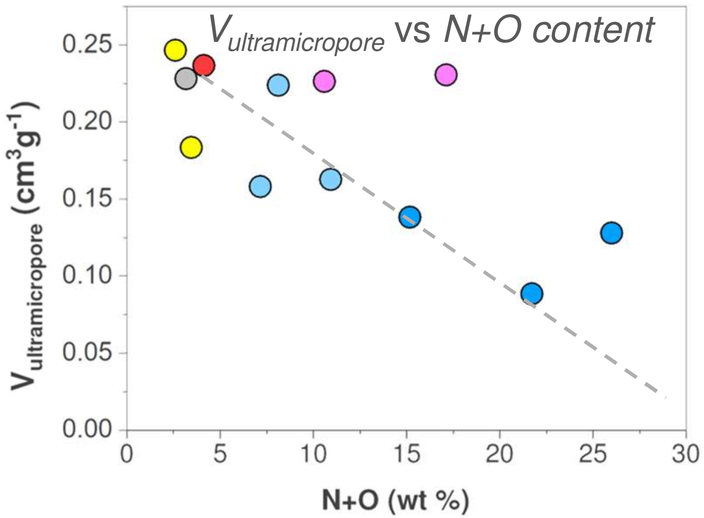
These treatments were applied to tune the heteroatom content and surface chemistry

CENTRE DE PHYSIQUE DES PARTICULES DE MARSEILLE
CPPM

Textural and chemical trends for C12-based carbons







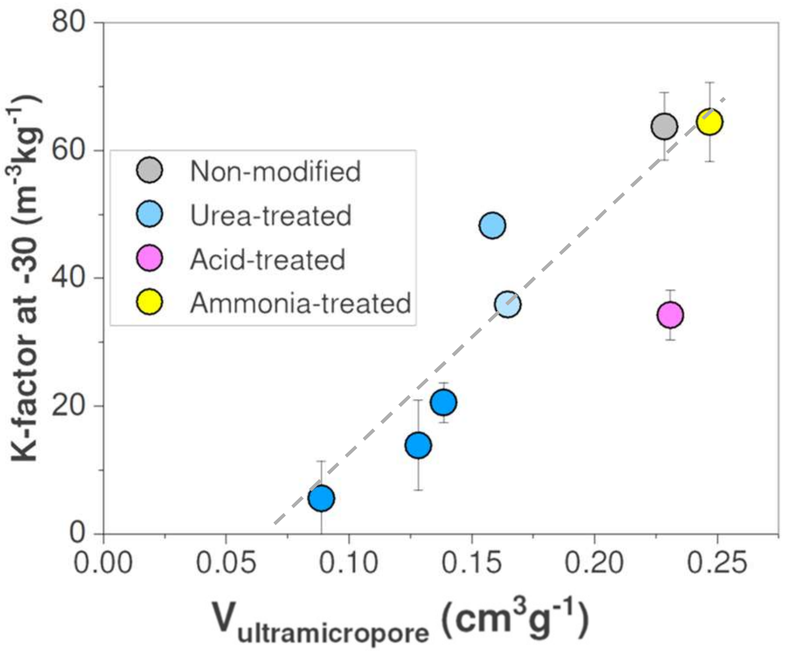
Ultramicropore volume increases with increasing $\mathbf{A_{BET}}$

Higher N+O contents tend to **reduce ultramicroporosity**

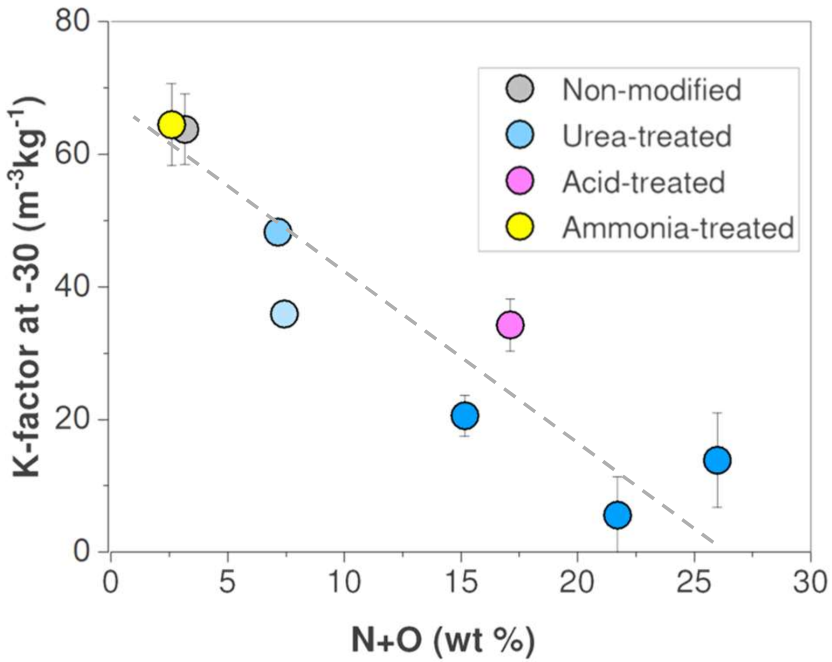
O-U2 (**oxidized + urea**) materials display the **lower ultramicropore volume**

K-factor trends for C12-based carbons

K-factor vs $V_{ultramicropore}$



K-factor vs N+O content



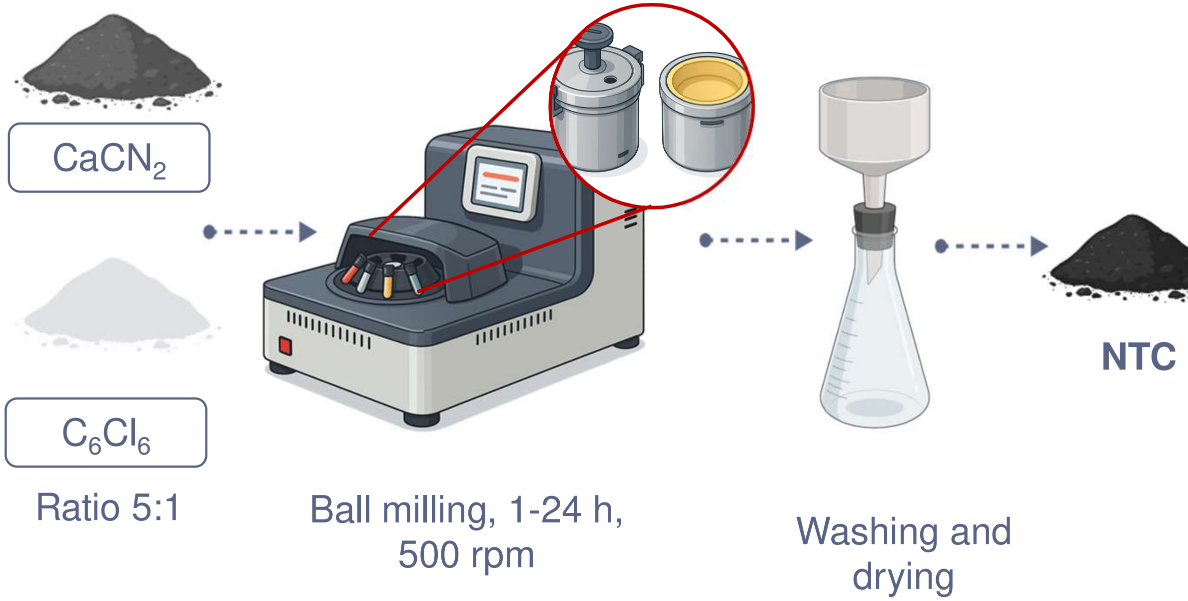
K-factor is primarily governed by $\mathbf{V_{<0,7nm}}$ in C12-based carbons

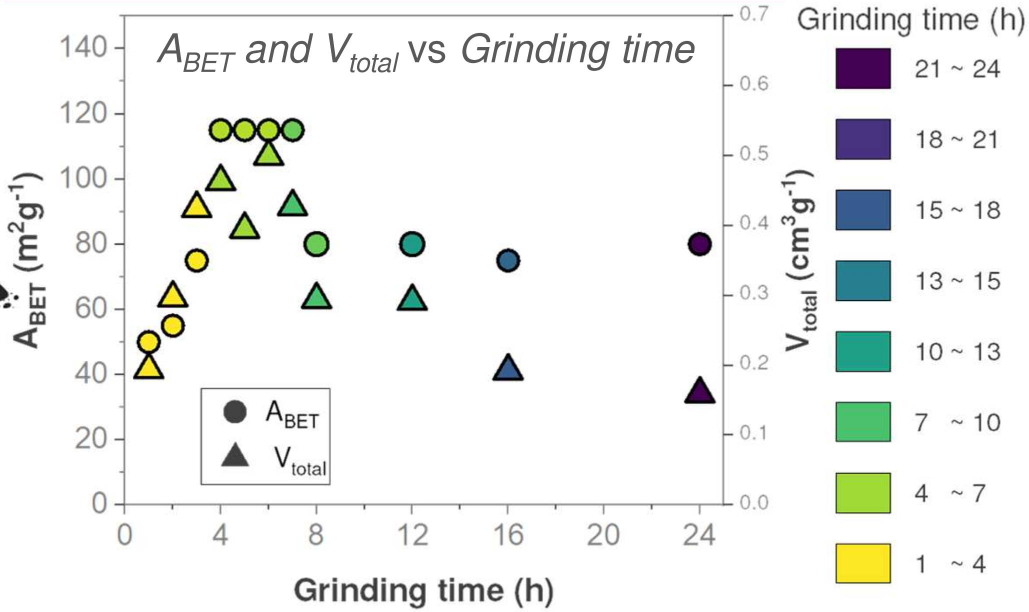
Samples with **higher N+O** contents show **lower K-factors** because $V_{<0,7nm}$ decreases upon doping

Heteroatom enrichment could, in principle, **improve Ag dispersion**

Can **Ag loading offset** the performance loss induced by N+O doping?

Nitrogen-containing turbostratic carbon





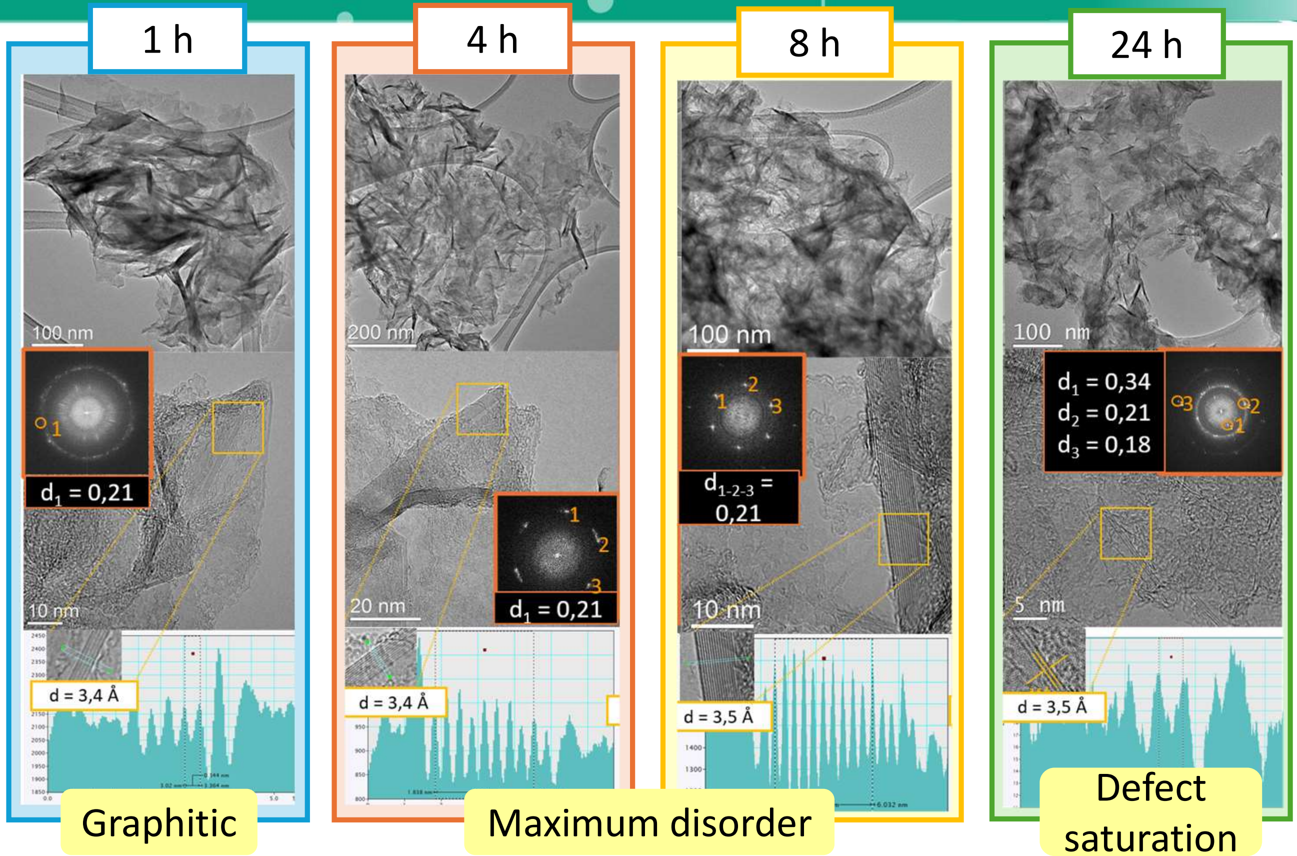
Mechanosynthetic route, with ball milling as the driving force

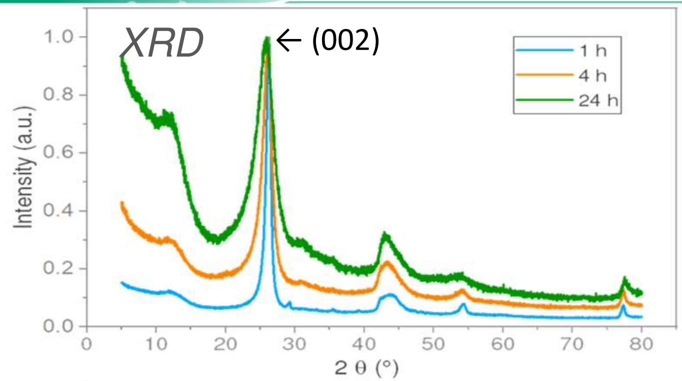
Predominantly **mesoporous** carbon materials, **low $V_{<0,7\ nm}$**

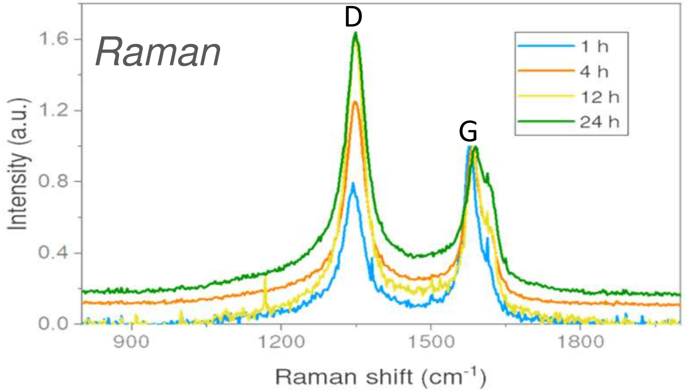
Limited BET area (**< 120 m² g⁻¹**)

Possibility of **Ag doping**; already performed and samples sent

Structural Evolution of NTC







Intermediate milling times (4–8 h) correspond to the **maximum-disorder regime**

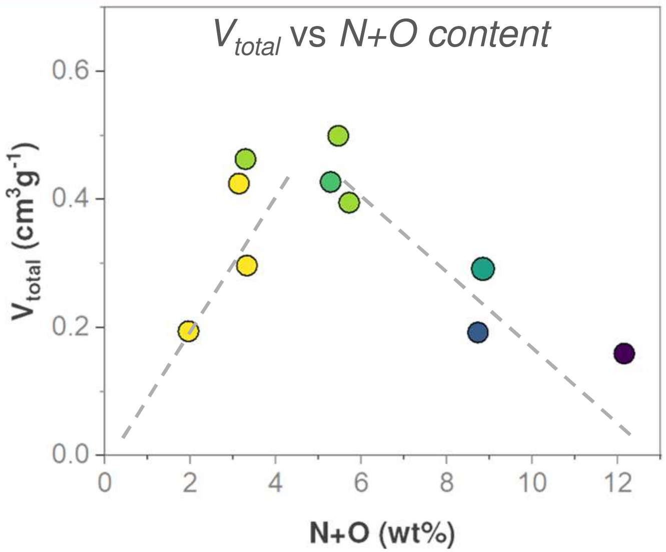
At 24 h, Raman and XRD indicate a highly defective state with **defect saturation**

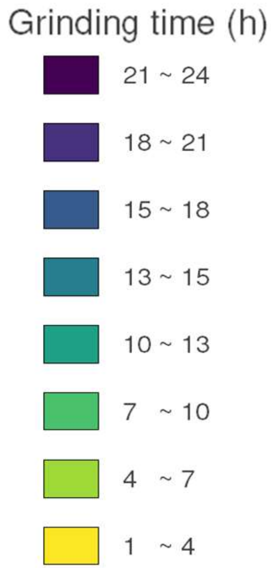
Materials with **larger graphitic domains** at room temperature

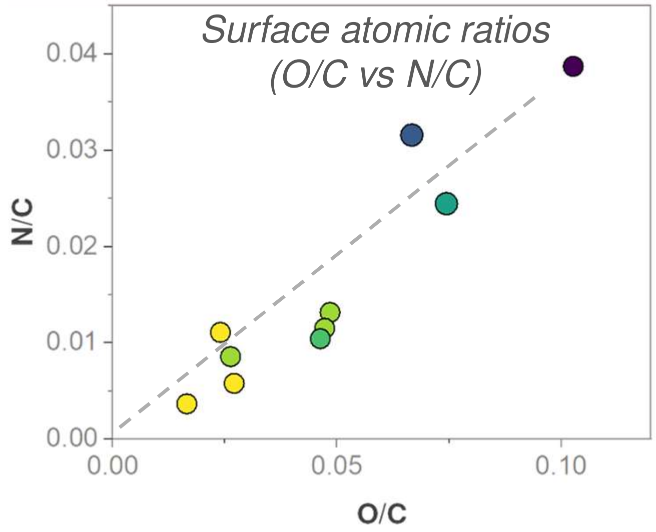
Raman defect metrics

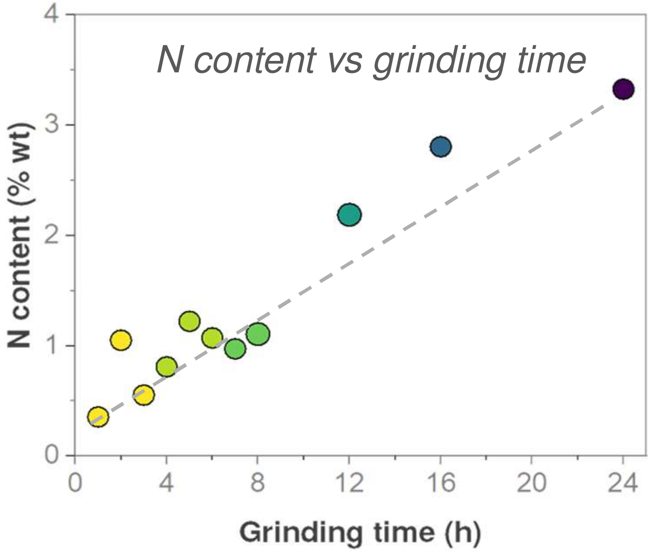
Time	ID/IG	La (nm)
1 h	0.80	~24
4 h	1.25	~15
8 h	1.70	~11
24 h	**1.64**	**~12**

Surface chemistry evolution of NTC







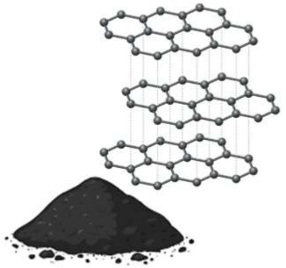


Total pore volume does **not** follow a simple trend with **N+O content**

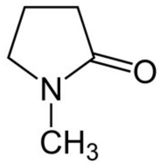
N content increases with grinding time

O/C and N/C ratios increase together → **progressive** surface modification

Synthesis of Ag-loaded graphite by ball milling



Graphite, 0.2 g



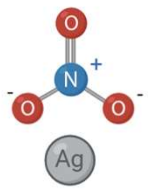
NMP, 5 ml

Graphite exfoliation

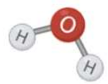
Ball milling, 3 h, 500 rpm

Centrifugation, 20 min, 1000 rpm

Collected supernatant, 5 ml



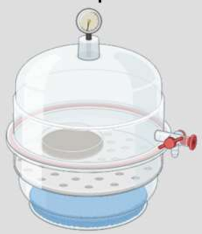
$AgNO_3$, 0.03 g



Distilled water, 0.5 ml

Ag loading

Ball milling, 3 h, 500 rpm



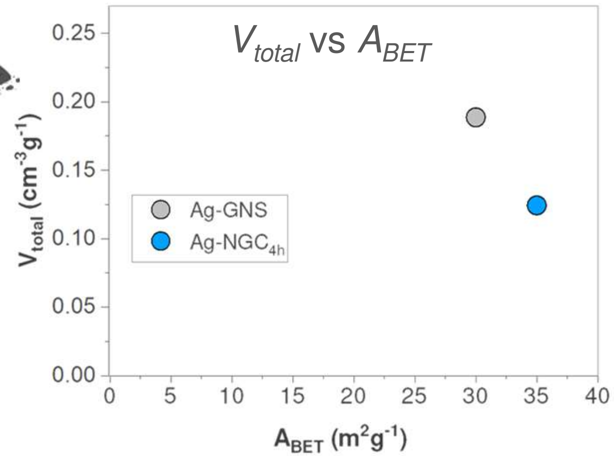
Washing with water and ethanol

Vacuum drying, RT, 24 h

Ag-loaded graphite

SAMPLE	CODE
Ag-loaded graphite	**Ag@GNS**
Ag-loaded NGC *	**$Ag@NTC_{4h}$**

*N-containing turbostratic carbon (**NTC**) prepared by mechanosynthesis from $CaCN_2$ and C_6Cl_6

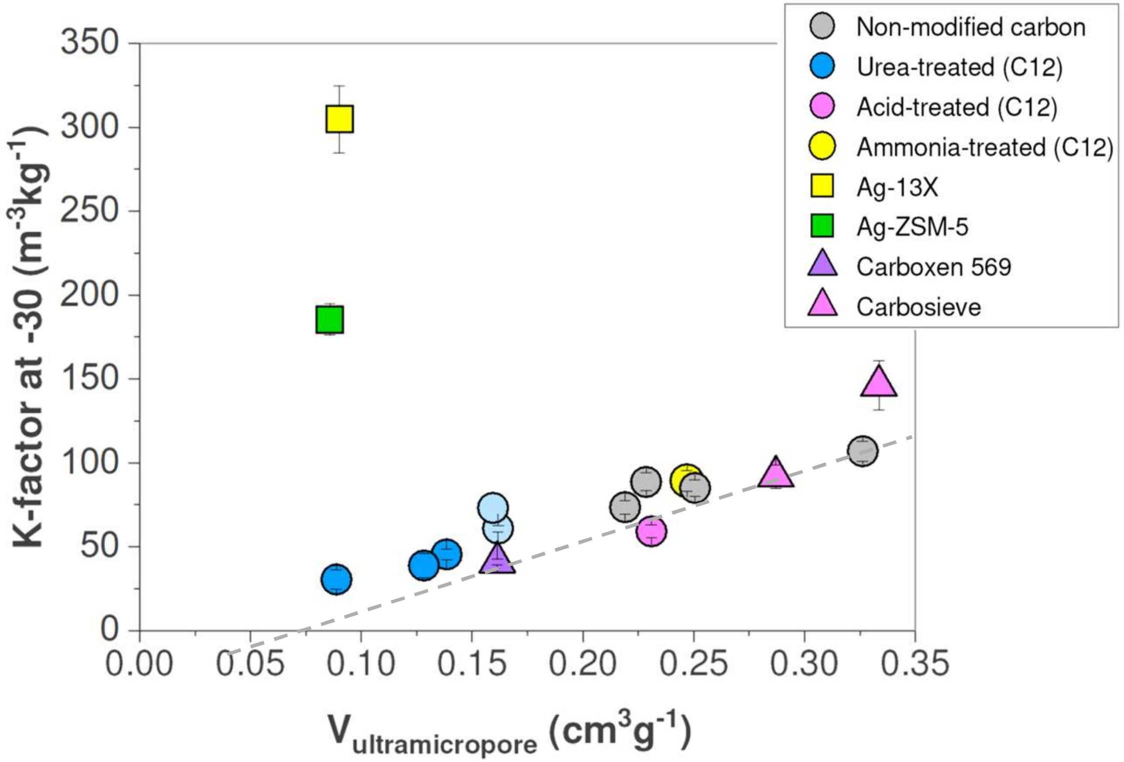


2 samples → CPPM

CENTRE DE PHYSIQUE DES PARTICULES DE MARSEILLE
CPPM

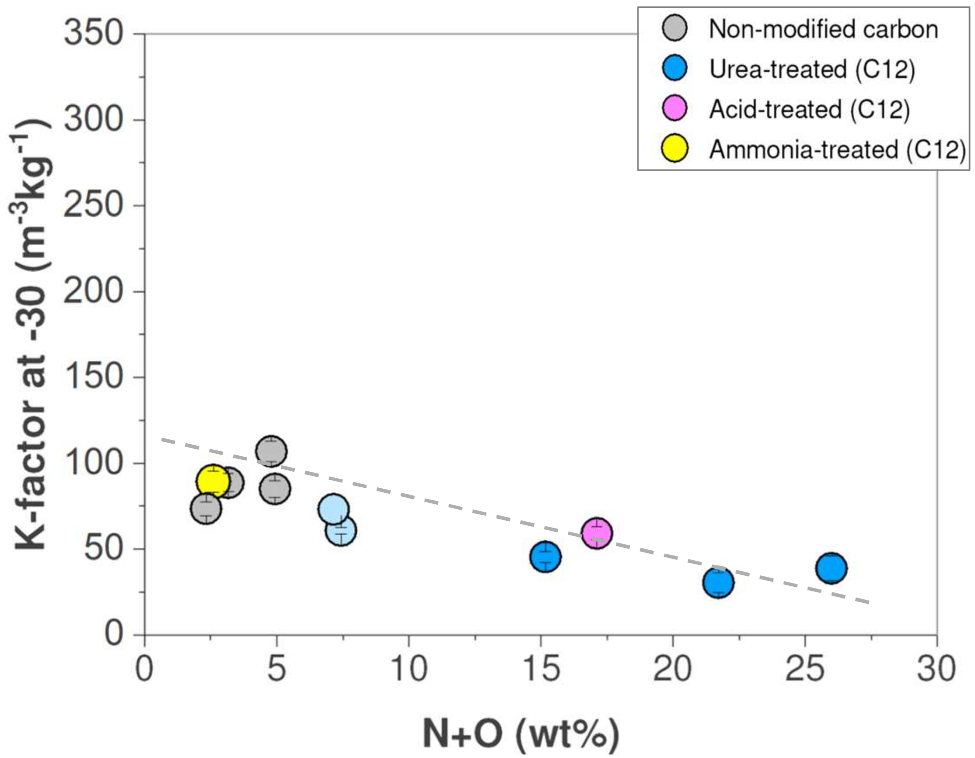
K-factor vs structure and chemistry

K-factor vs $V_{ultramicropore}$



Across **carbon materials**, K-factor **increases** with increasing $\mathbf{V_{<0,7\ nm}}$

K-factor vs N+O content

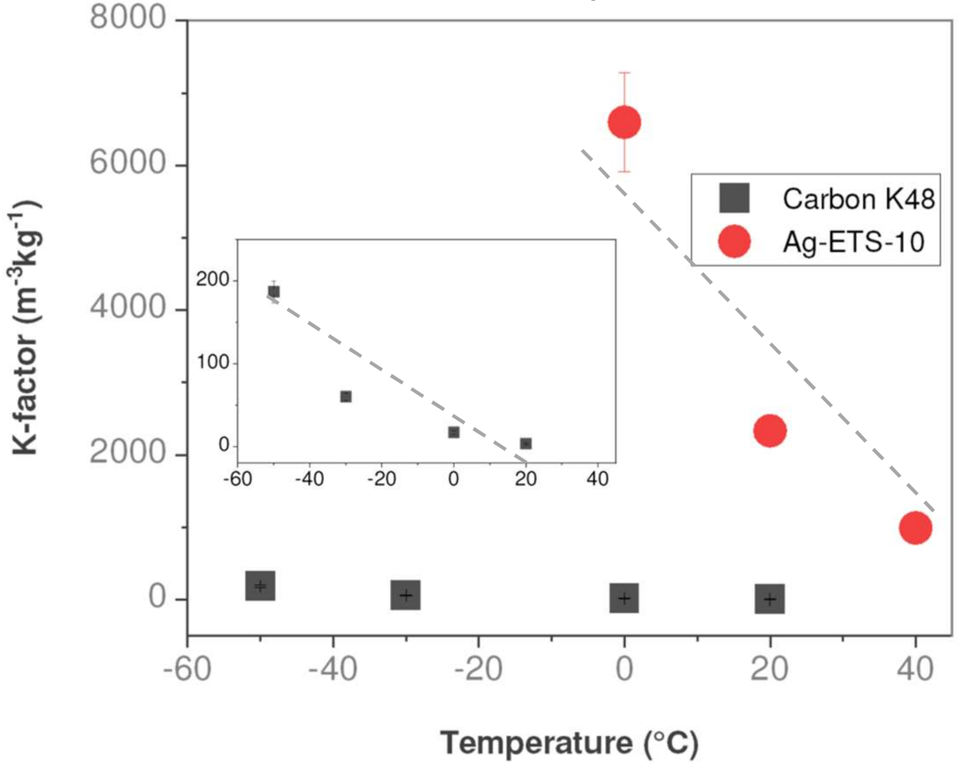


No positive correlation is observed between K-factor and **N+O content**

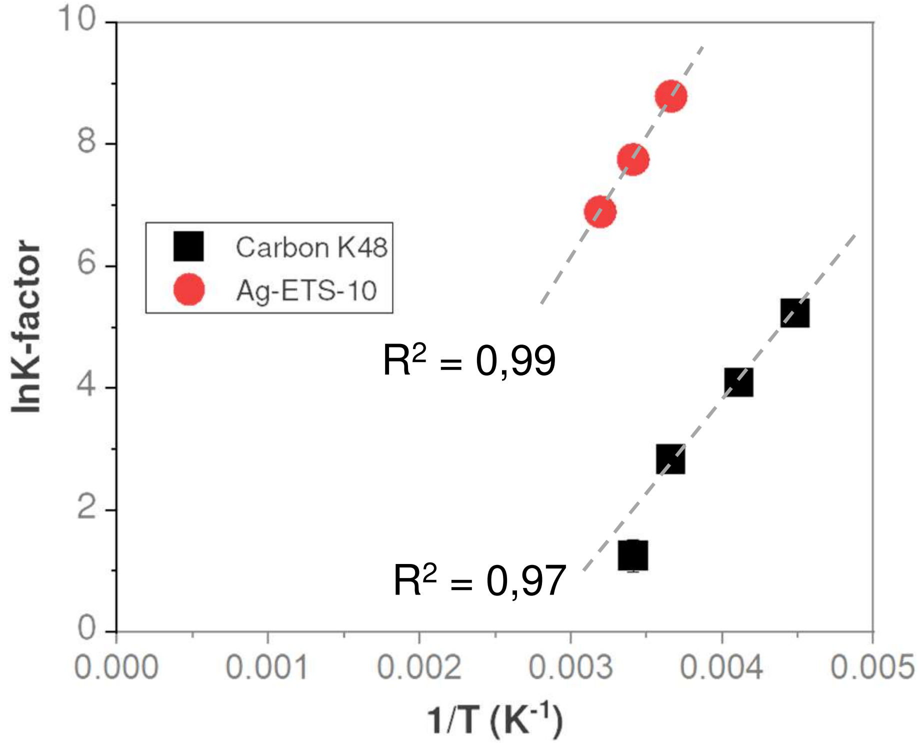
In this dataset, the **effect of chemical doping** on the **K-factor** is mainly conveyed through changes in $\mathbf{V_{<0,7\ nm}}$

Temperature dependence of the K-factor

K-factor vs Temperature



Arrhenius-type representation of K-factor



K-factor increases at decreasing **temperature**, for both materials tested

Ln(K-factor) shows a linear dependence on **1/T** (Arrhenius-type behavior, $\mathbf{R^2 \geq 0.97}$)

This suggests that **K-factor** is governed by an activated process, consistent with an Arrhenius-type **dependence on temperature**

ASAP 2020 Plus

cryoTune 87

Single-gas adsorption isotherms measured by **volumetric adsorption**

Cryogenic **temperature control** using cryoTune

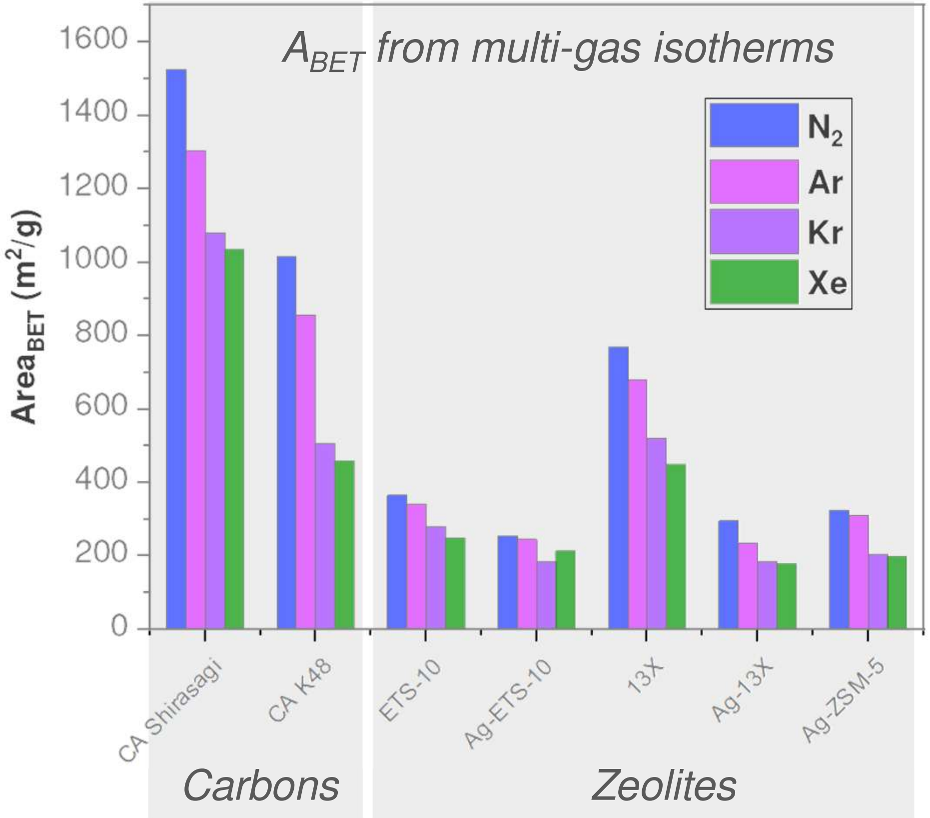
Multi-gas isotherms **disentangle textural** and **chemical** effects in Rn adsorption

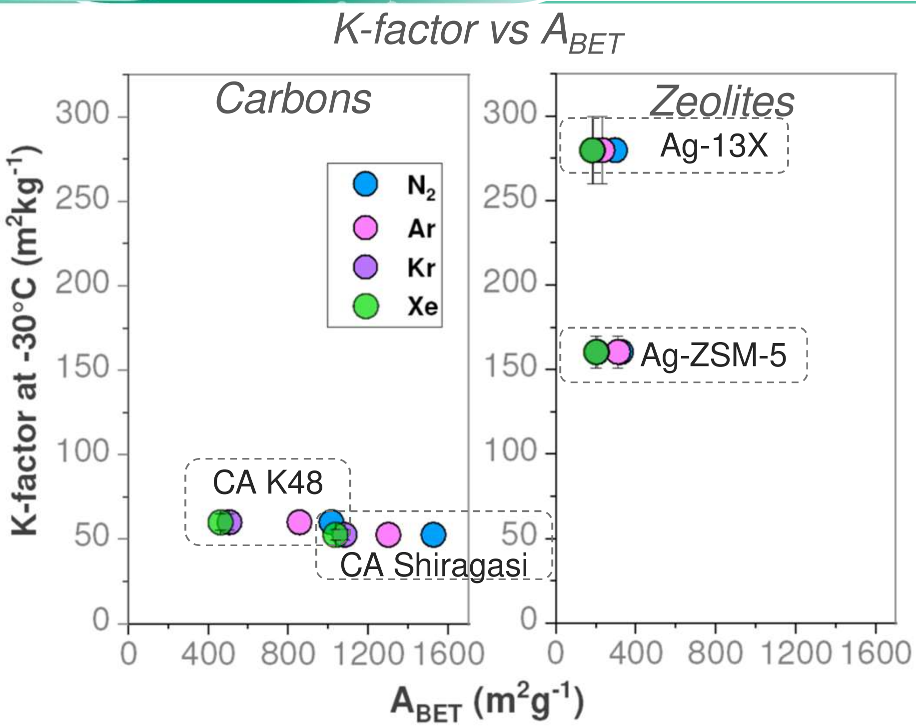
Gas	Analysis temperature (K)	Cross-sectional value σ (Å²)
N_2	77	16.2
Ar	87.3	14.2
Kr	119.7	13.7
Xe	165	16.8

Argon at **87.3 K** has a kinetic diameter **of ≈3.4 Å**; this effective size is essentially the same at the K-measurement temperature

$Area_{BET}$ from Multi-Gas Isotherms

Gas (Analysis temperature, K)	N2 (77K)	Ar (87,3)	Kr (119,7K)	Xe (165 K)
Cross-sectional value (Å)	16.2	14.2	13.7	16.8





A_{BET} depends on the **probe gas** used for the isotherm analysis

K-factor – A_{BET} relationships should be discussed within each material family, not across different families

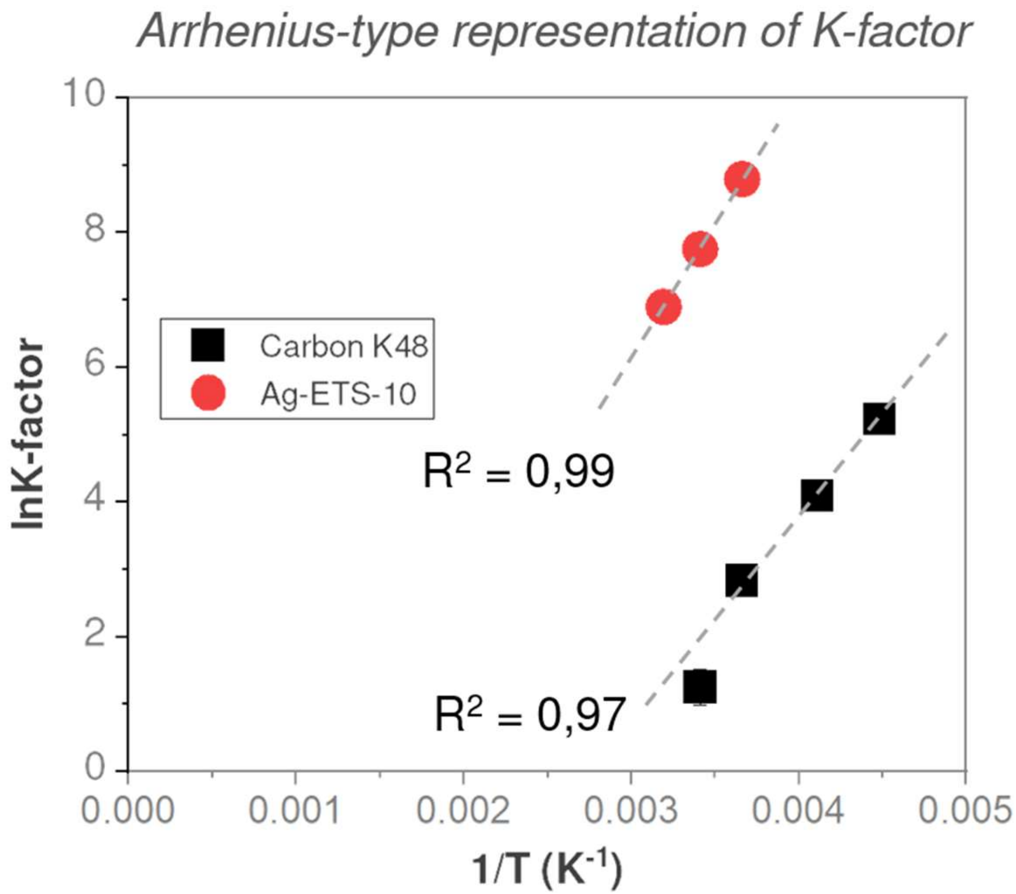
Additional K-factor data are needed for all materials characterized with multiple probe gases

Key observations

For **carbon materials**, K-factor **increases** with increasing **$V_{< 0.7\ nm}$**

Chemical doping (N+O) **modifies surface chemistry** but often **reduces $V_{< 0.7\ nm}$**, leading to **lower K-factors** in C12-based carbons

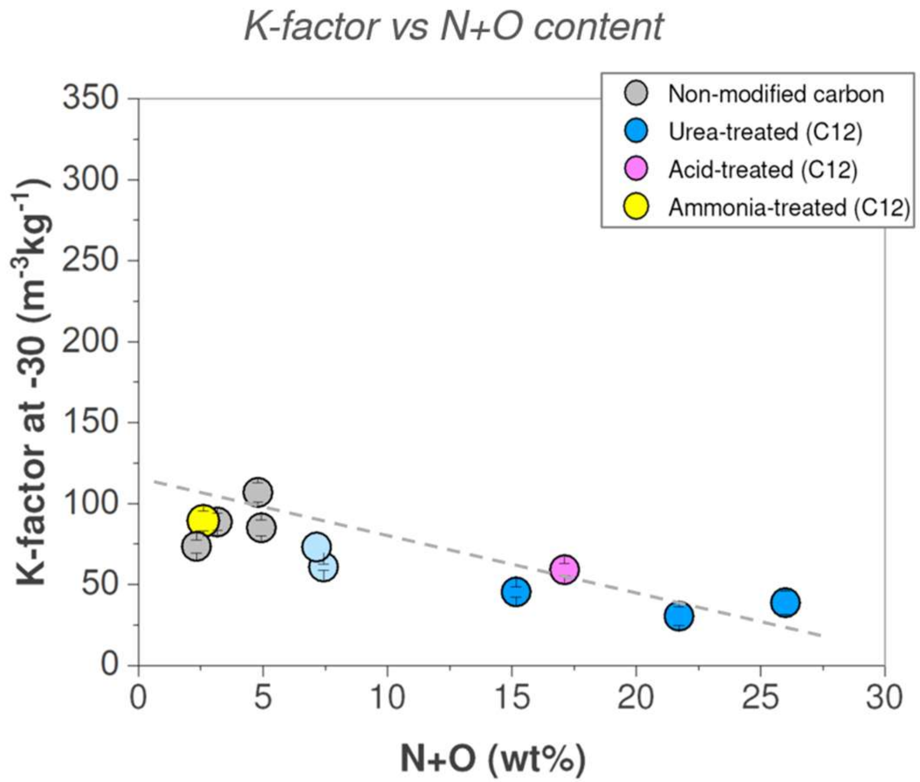
K-factor also **increases** as **temperature decreases**, with ln(K) showing an Arrhenius-type dependence on 1/T



Ongoing **review** on **noble gas adsorption** in porous materials

Investigate **temperature effects** on adsorption behavior

Complement textural analysis with targeted **chemical characterization**



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Thank you for your attention