Solid-state NMR studies of nanoporous carbons

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Outline

- **Porous carbons: properties and methods of synthesis.**
- **Surface groups in porous carbons.**
- **Multinuclear magnetic resonance studies.**
- **Recent results of NMR studies of nanoporous carbons.**
- **Conclusion.**

Research on Carbon Materials in Vitória

Laboratory of Carbon and Ceramic Materials (LMC)

Federal University of Espírito Santo, Vitória, Brazil

http://www.cce.ufes.br/dfis/lmc.htm

Some materials of interest:

- ✓ Chars produced from natural resources (peat, rice hulls, coconuts, etc).
- ✓ Carbon blacks produced by plasma pyrolysis of natural gas.
- ✓ Plasma modified vacuum residues of oil refinement.
- ✓ Activated carbons.
- ✓ Composites of porous carbons and magnetic nanoparticles.

Some characterization techniques:

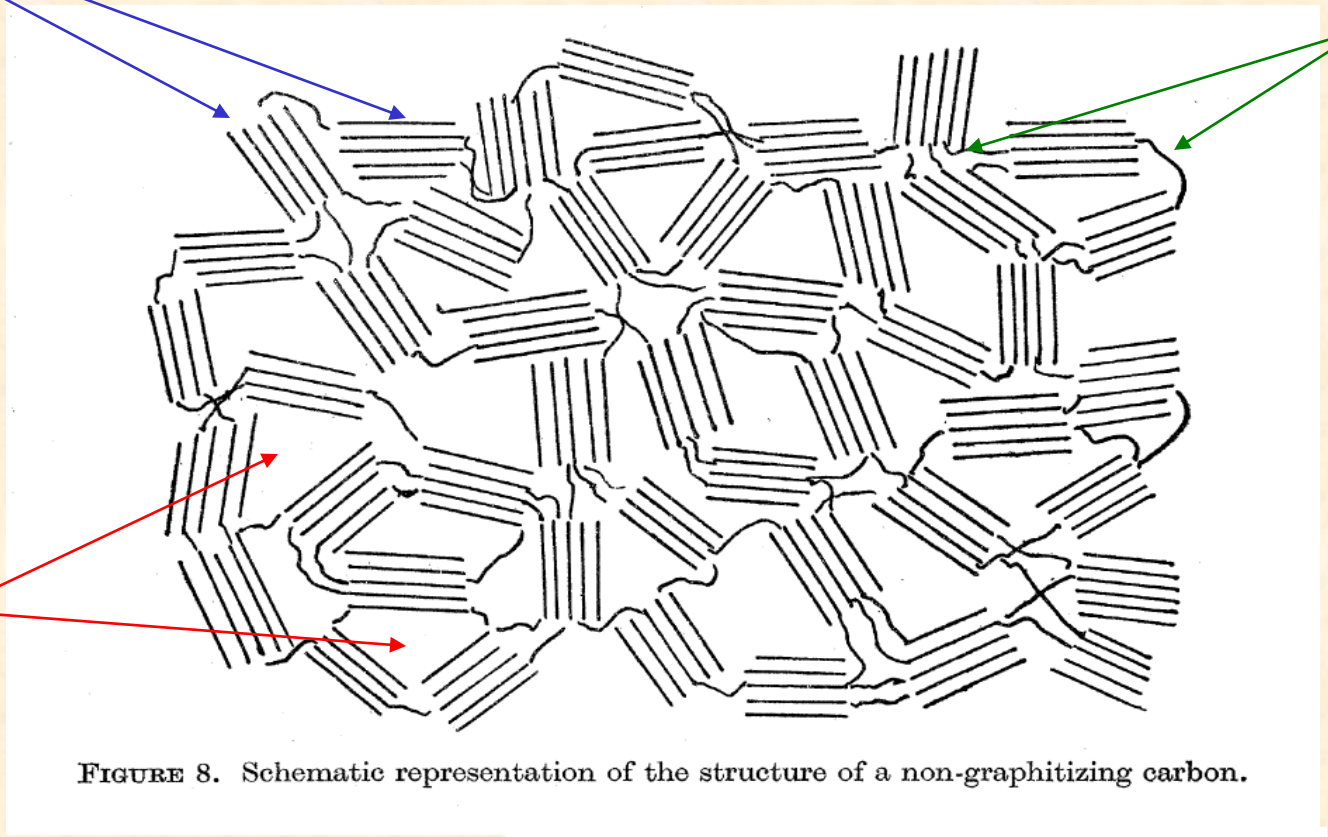
- ✓ XRD, SEM, NMR (^{13}C, ^{29}Si, etc), Mössbauer spectroscopy, TG, DSC, CHNSO analysis, etc.
- ✓ Textural properties (BET surface area, pore size distribution, true density, etc).
- ✓ Physical properties (electrical resistivity, magnetic susceptibility, etc).

Structure of disordered carbons

Graphite-like crystallites

Franklin model

Cross-links



Pores

FIGURE 8. Schematic representation of the structure of a non-graphitizing carbon.

R. E. Franklin, *Proc. Roy. Soc. London A* 1951;209:196

Composition: C, H, O (major), N, S, ashes,...

Activated carbons

- Disordered solids with irregular porous network.
- Presence of macropores, mesopores and micropores.
- Applications: catalysis, water treatment, gas storage, ...
- Basic constitution: C, H, O (major), N, S, ...
- Mineral fraction: depends on the precursor.

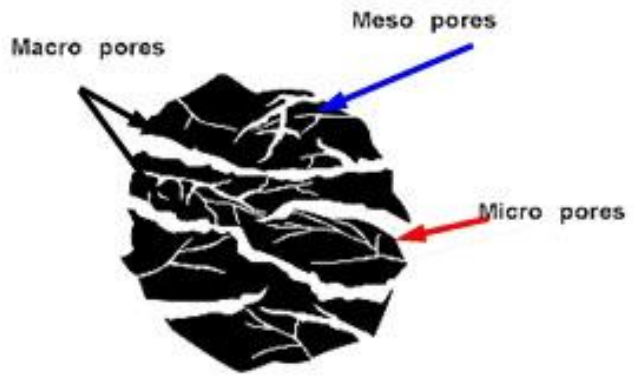


Figure 1: Activated carbon structure - schematic.

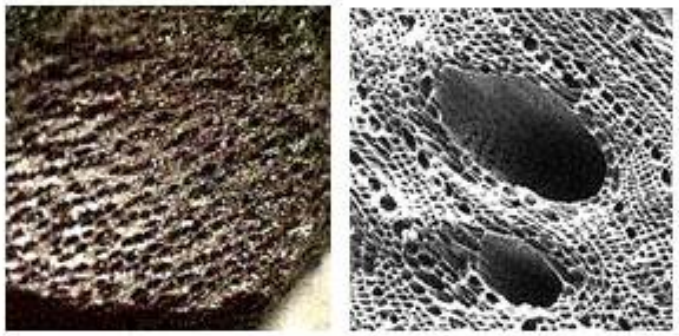


Figure 2: Activated carbon structure – SEM pictures.

http://www.afssociety.org/education/0209oneminute.html

Activated carbons

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- Applications: catalysis, water treatment, gas storage, ...
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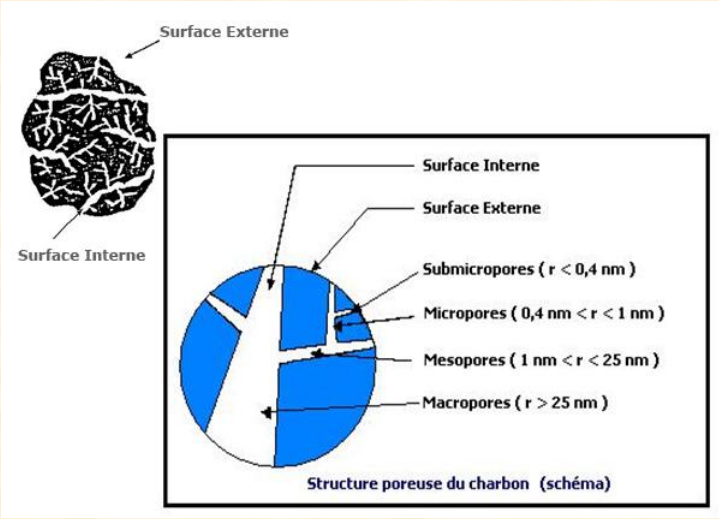
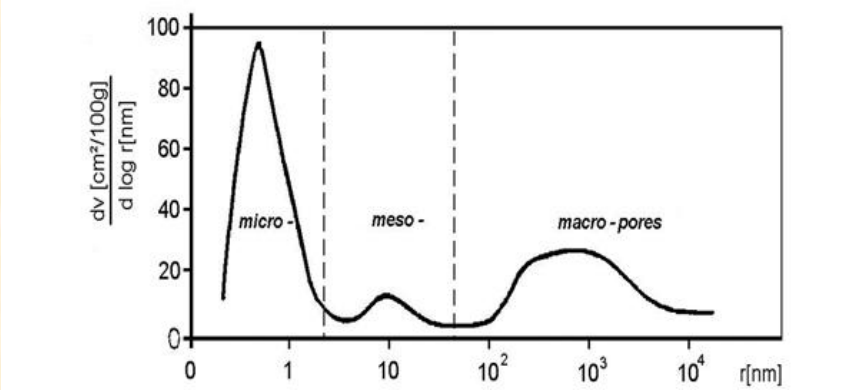




http://www.asseau.com/en/03-9.html

Activated carbons

– Manufacture:

- Physical activation: steam, air, CO_2,…
- Chemical activation: H_3PO_4, NaOH, KOH, $CaCl_2$, …
- Precursors: coal, anthracite, chars, lignocellulosic materials, …
- Heat-treatments, washing, drying, chemical post-treatments, …
- Presence of "inorganic" elements: Na, K, Ca, P, …
  - ✓ Associated with mineral matter in the precursor and with the reactants used in chemical activation.
  - ✓ Affect the surface chemistry of the porous carbons.

Surface groups in porous carbons

- Oxygen in surface functional groups influences most of the properties of porous carbons.

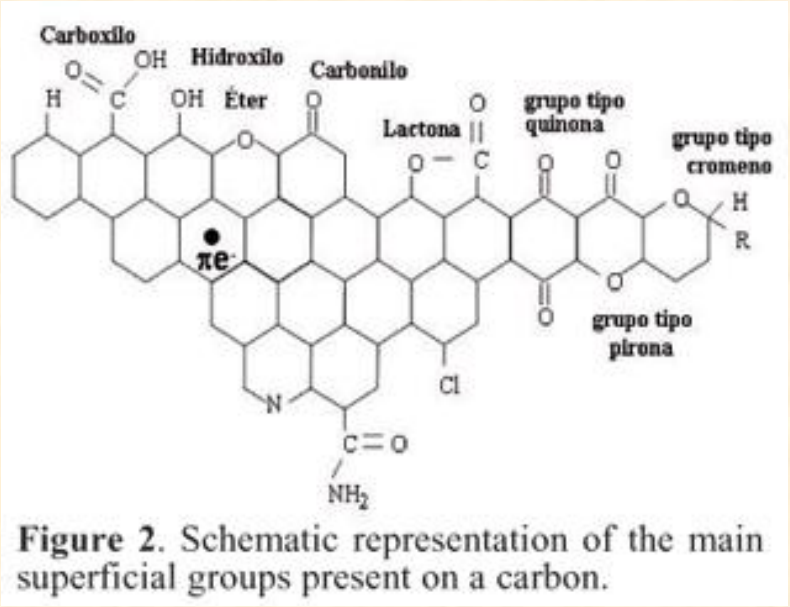
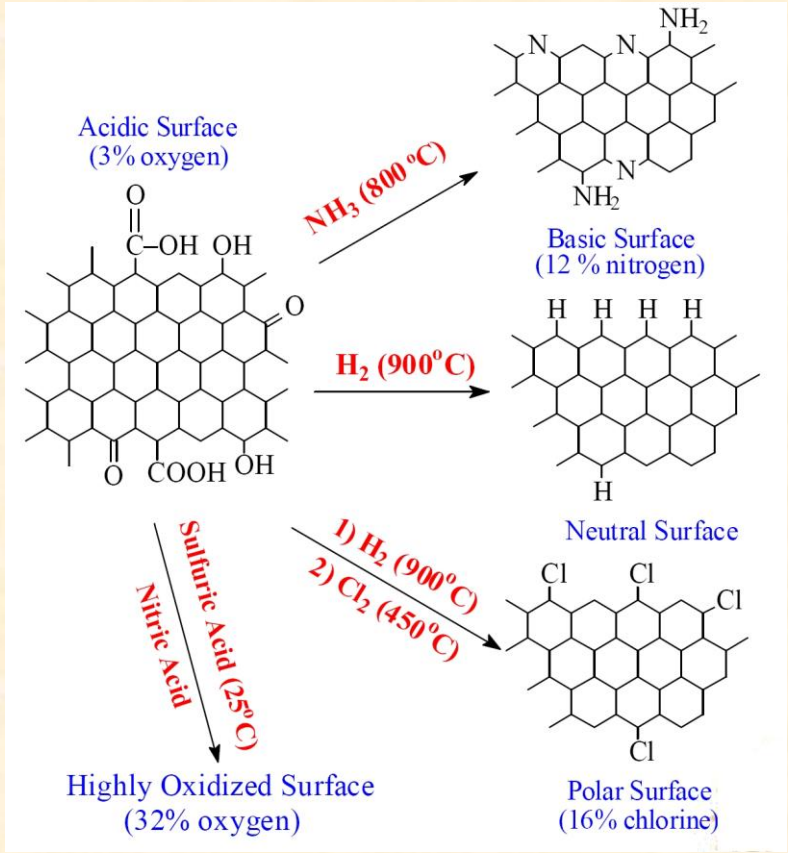


Figure 2. Schematic representation of the main superficial groups present on a carbon.

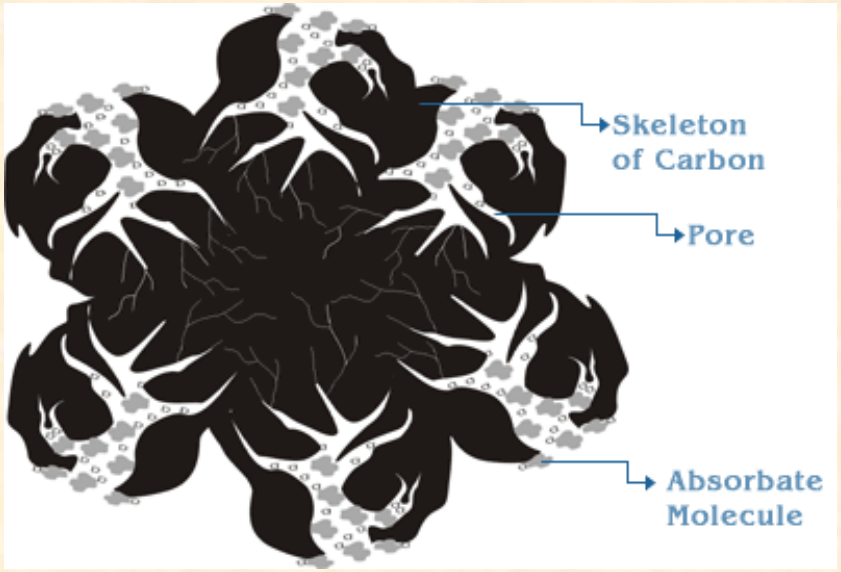


Cárdena-López et al., *Ecl. Quim. 2007;*32:61

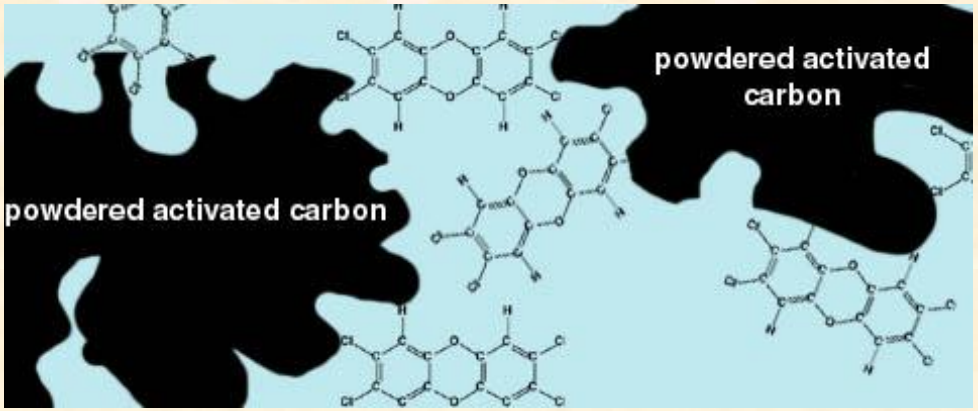
http://economy.matse.illinois.edu/figure/Economy-ACS.pdf

Surface groups in porous carbons

- Influence of surface groups on adsorption:



http://www.activatedcarbonindia.com/activated_carbon.htm



http://www.chemistry.wustl.edu/~courses/genchem/Tutorials/Water/Adsorption.htm

Surface groups in porous carbons

On the Chemical Nature of Graphene Edges: Origin of Stability and Potential for Magnetism in Carbon Materials

Ljubisa R. Radovic*,† and Bradley Bockrath‡

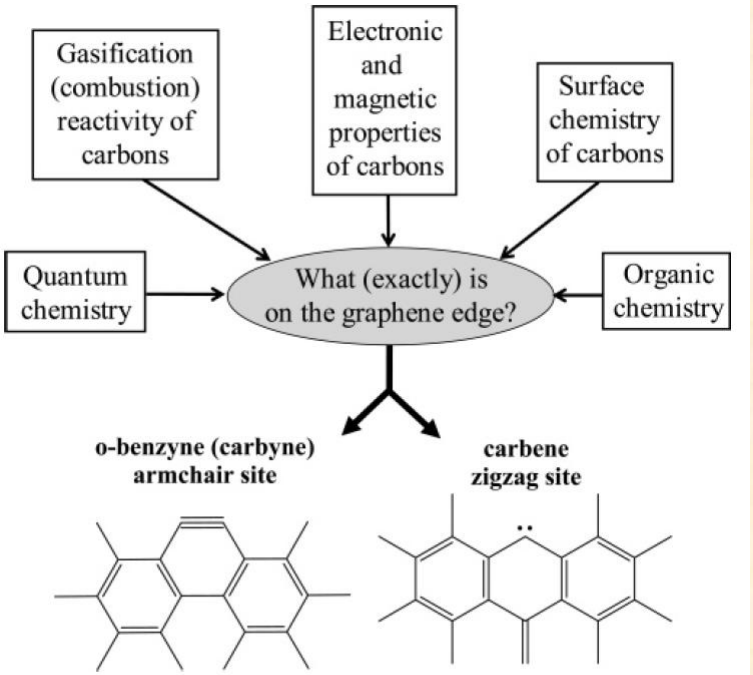


Figure 1. Proposal for the chemical nature of free edge sites in sp^2-hybridized carbons, based on current understanding of chemistry and physics of carbon materials.

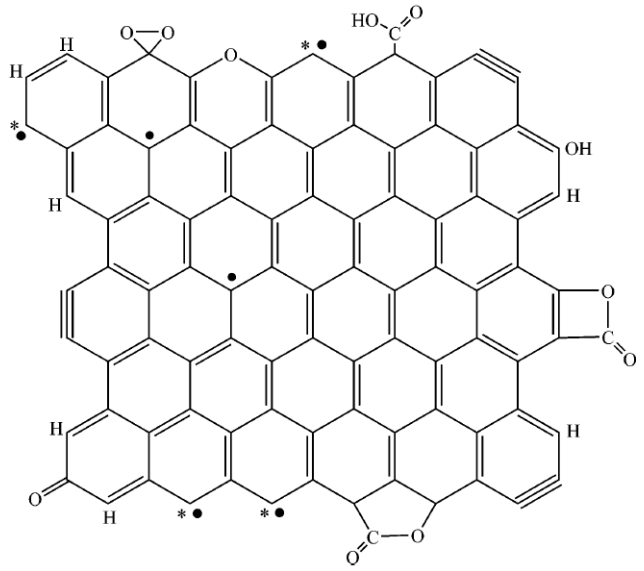


Figure 2. Schematic representation of the main chemical features in a graphene sheet, with its typical surface functionalities, and including the free edge sites. The pairing of σ (*) and π (●) electrons at the zigzag sites and the presence of triple bonds at the armchair sites is indicated. The abundance of aromatic sextets and the degree of π electron delocalization depends on size, shape. and connectivity of the graphenes, as well as on their edge termination.

Radovic & Bockharth, *J. Am. Chem. Soc.* 2005;127:5917

Surface groups in porous carbons

- Characterization methods: Titration, FT-IR, XPS, TPD, NMR, etc.
- Advantages of solid-state NMR: Boehm, *Carbon* 2002;40:145
  - ✓ Non-destructiveness.
  - ✓ Element-selective technique.
  - ✓ Sensitiveness to chemical environment and to structural features around the nuclear site.
- Main drawback:
  - ✓ Little sensitiveness to nuclei in surface groups.

Solid-state NMR studies

Some nuclides of interest for studies of porous carbons:

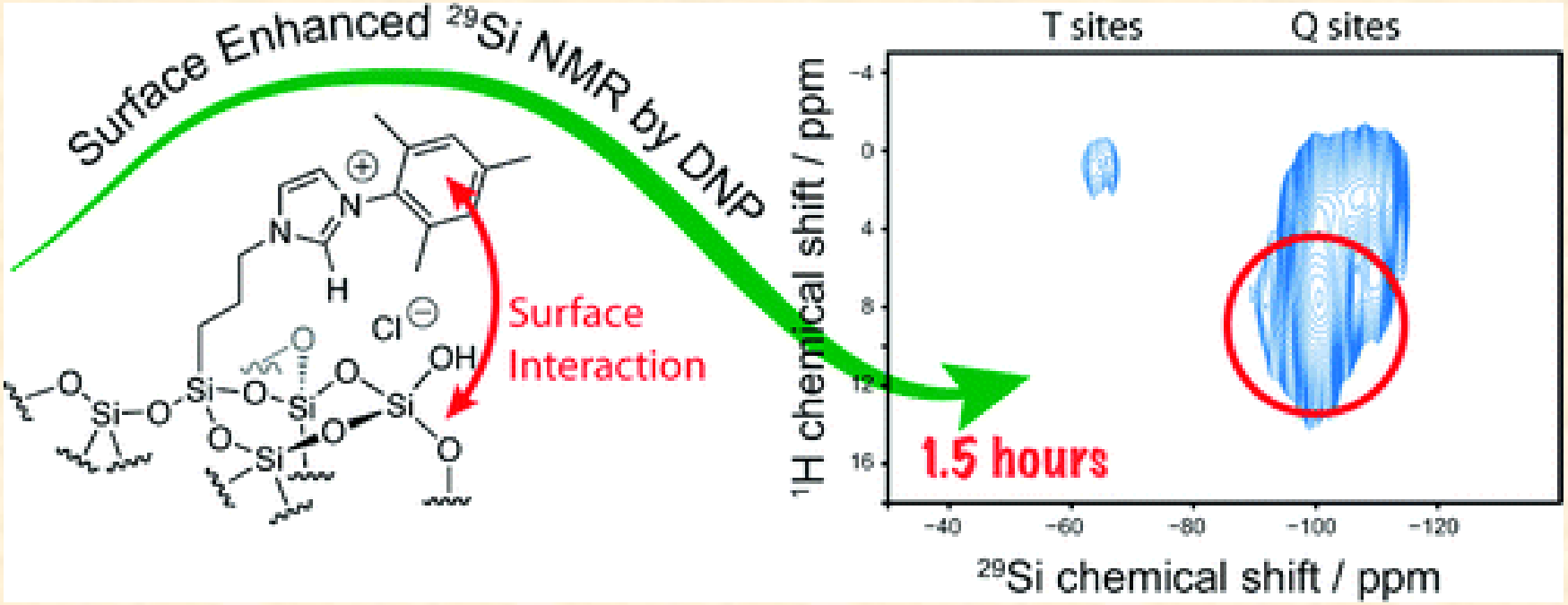
Nuclide	*Natural abundance* (%)	*Nuclear spin*	*Larmor frequency* [a] (MHz)	*Sensitivity* [b]
^{1}H	99.99	1/2	100.000	1.000
^{13}C	1.07	1/2	25.145	1.70×10^{-4}
^{14}N	99.632	1	7.226	1.00×10^{-3}
^{17}O	0.038	5/2	13.556	1.11×10^{-5}
^{23}Na	100	3/2	26.452	9.27×10^{-2}
^{29}Si	4.683	1/2	19.867	3.68×10^{-4}
^{31}P	100	1/2	40.481	6.65×10^{-2}
^{33}S	0.76	3/2	7.676	1.72×10^{-5}
^{39}K	93.258	3/2	4.666	4.76×10^{-4}
^{43}Ca	0.135	7/2	6.730	8.68×10^{-6}
^{129}Xe	26.44	1/2	27.810	5.72×10^{-3}

[a] Corresponding to the magnetic field of 2.35 T of a 100 MHz NMR spectrometer.
[b] Relative to ^{1}H.

Harris et al., *Pure Appl. Chem.* 2001;73(11):1795-1818

Solid-state NMR studies

Surface enhanced NMR using dynamic nuclear polarization:



Emsley et al., *J. Am. Chem. Soc.* 2011;133:2104

Incipient wetness impregnation of the porous material (silica) with a solution containing the polarizing radical.

Synthesis of the AC samples

Lignocellulosic precursor

Rice hulls, coffee husk, testa of oil seeds, peat, etc.

↓

Carbonization

400-500°C, 0.5-4h, N_2 flow.

↓

Impregnation in aqueous medium

H_3PO_4, NaOH, KOH, $CaCl_2$, $ZnCl_2$, $FeCl_3$ etc.

↓

Activation heat-treatment

400-900°C, 0.5-2h, N_2 or air flow.

↓

Washing

Distilled water, methanol, acids, etc.

Porous carbon material

Characterization:

- Elemental analysis.
- Thermal analysis.
- N_2 sorption.
- SEM, XRD.
- Solid-state NMR

  ^{13}C, ^{23}Na, ^{29}Si, ^{31}P, ^{39}K, ...

Properties of the AC samples

Alkali-activated carbons (testa of oil seeds):

Label	Precursor	Chemical Agent / Wt. Ratio	Temp. / Atmosphere	Washing	SSA m^2/g	C wt. %	H wt. %	N wt. %	O wt. %	Diff. wt. %
DB3	NOS	None	550°C Closed	Water HNO_3 MeOH	14	64.2	2.9	2.7	28.6	1.5
DB5	NHS	None	550°C Closed	Water HNO_3 MeOH	15	65.5	2.9	2.8	28.1	0.6
DB6	NHS	KOH 4:1	950°C N_2	Water HNO_3 MeOH	690	54.7	3.4	0.8	36.8	4.4
DB7	NHS	KOH 4:1	950°C Air	Water HNO_3 MeOH	763	57.1	3.1	0.8	33.4	5.5
DB8	NOS	KOH 1:1	850°C N_2	Water HNO_3 MeOH	851	62.6	3.0	0.7	31.6	2.1
DB9	NOS	KOH 2:1	850°C N_2	Water HNO_3 MeOH	657	56.1	3.2	0.9	38.2	1.5
DB10	NOS	NaOH 1:1	850°C N_2	Water HNO_3 MeOH	456	73.0	2.2	0.7	17.6	6.5
DB11	NOS	NaOH 2:1	850°C N_2	Water HNO_3 MeOH	536	72.2	2.9	0.7	17.1	7.3

Properties of the AC samples

$CaCl_2$-activated carbons (testa of oil seeds):

Label	Precursor	Chemical Agent / Wt. Ratio	Temp. / Atmosphere	Washing	SSA m^2/g	C wt. %	H wt. %	N wt. %	O wt. %	Diff. wt. %
DB1	NOS	None	550°C Closed	Water MeOH	258	82.6	2.4	1.1	13.9	0.1
DB3	NOS	None	550°C Closed	Water HNO_3 MeOH	14	64.2	2.9	2.7	28.6	1.5
DB12	NOS	$CaCl_2$ 1:1	850°C N_2	Water HNO_3 MeOH	555	70.1	2.2	0.9	22.8	4.0
DB13	NOS	$CaCl_2$ 2:1	850°C N_2	Water HNO_3 MeOH	341	73.8	2.1	1.0	20.6	2.5
DB14	NOS	$CaCl_2$ 1:1	850°C Air	Water MeOH	188	76.7	1.8	0.8	13.6	7.2
DB15	NOS	$CaCl_2$ 2:1	850°C Air	Water MeOH	278	72.4	2.0	0.7	15.5	9.4
DB16	NOS	$CaCl_2$ 3:1	850°C Air	Water MeOH	273	70.8	2.0	0.7	17.0	9.4
DB17	NOS	$CaCl_2$ 4:1	850°C Air	Water MeOH	353	67.0	1.9	0.7	17.2	13.2

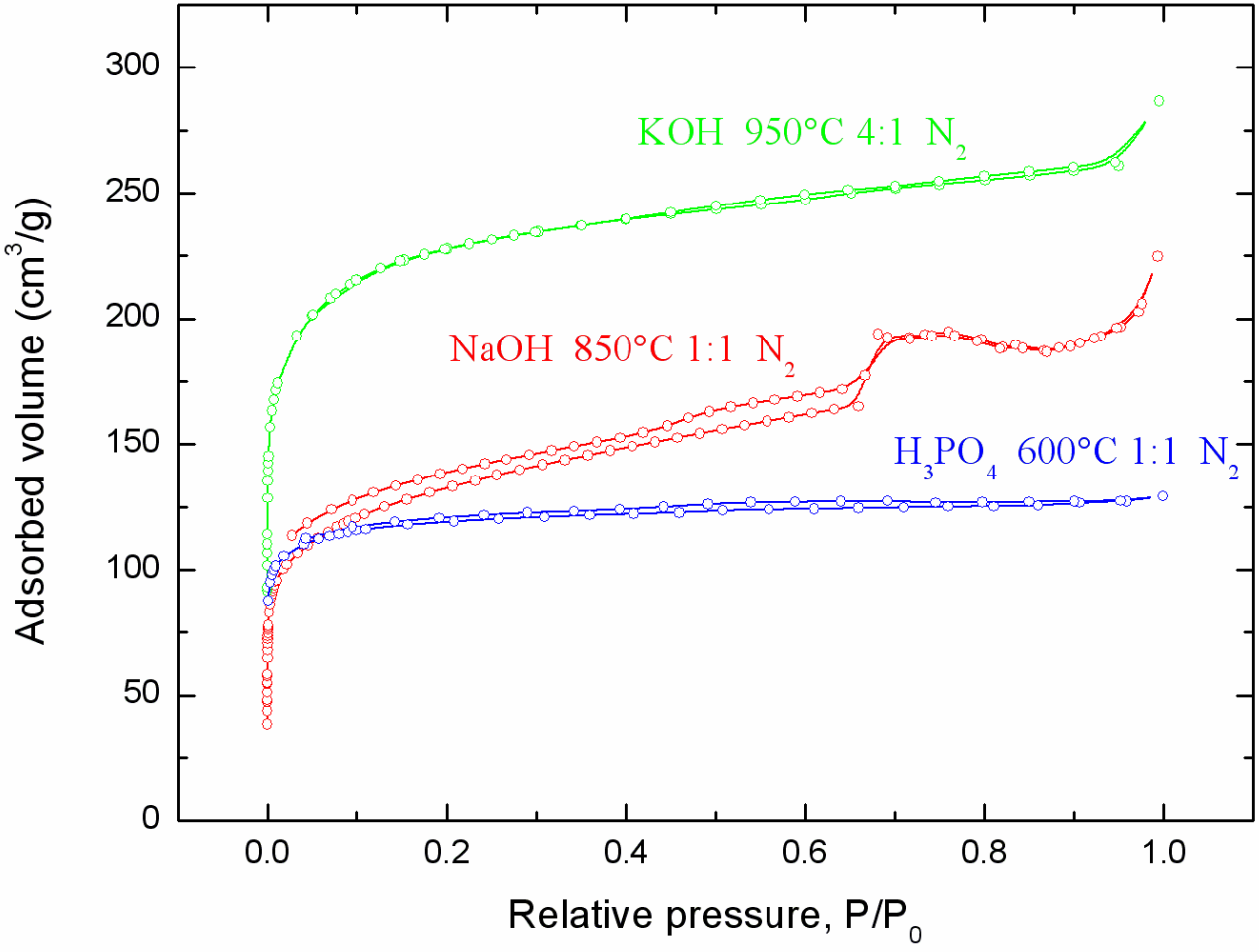
Properties of the AC samples

H_3PO_4-activated carbons (testa of oil seeds):

Label	Precursor	Chemical Agent / Wt. Ratio	Temp. / Atmosphere	Washing	SSA m^2/g	C wt. %	H wt. %	N wt. %	O wt. %	Diff. wt. %
DB1	NOS	None	550°C Closed	Water MeOH	258	82.6	2.4	1.1	13.9	0.1
DB18	NOS	H_3PO_4 1:1	500°C N_2	Water MeOH	341	74.3	2.9	1.1	19.4	2.4
DB19	NOS	H_3PO_4 1:1	600°C N_2	Water MeOH	399	69.7	2.7	1.1	23.0	3.6
DB20	NOS	H_3PO_4 1:1	700°C N_2	Water MeOH	434	70.5	2.7	1.0	22.3	3.5
DB21	NOS	H_3PO_4 1:1	800°C N_2	Water MeOH	1022	63.6	3.4	0.8	28.7	3.5

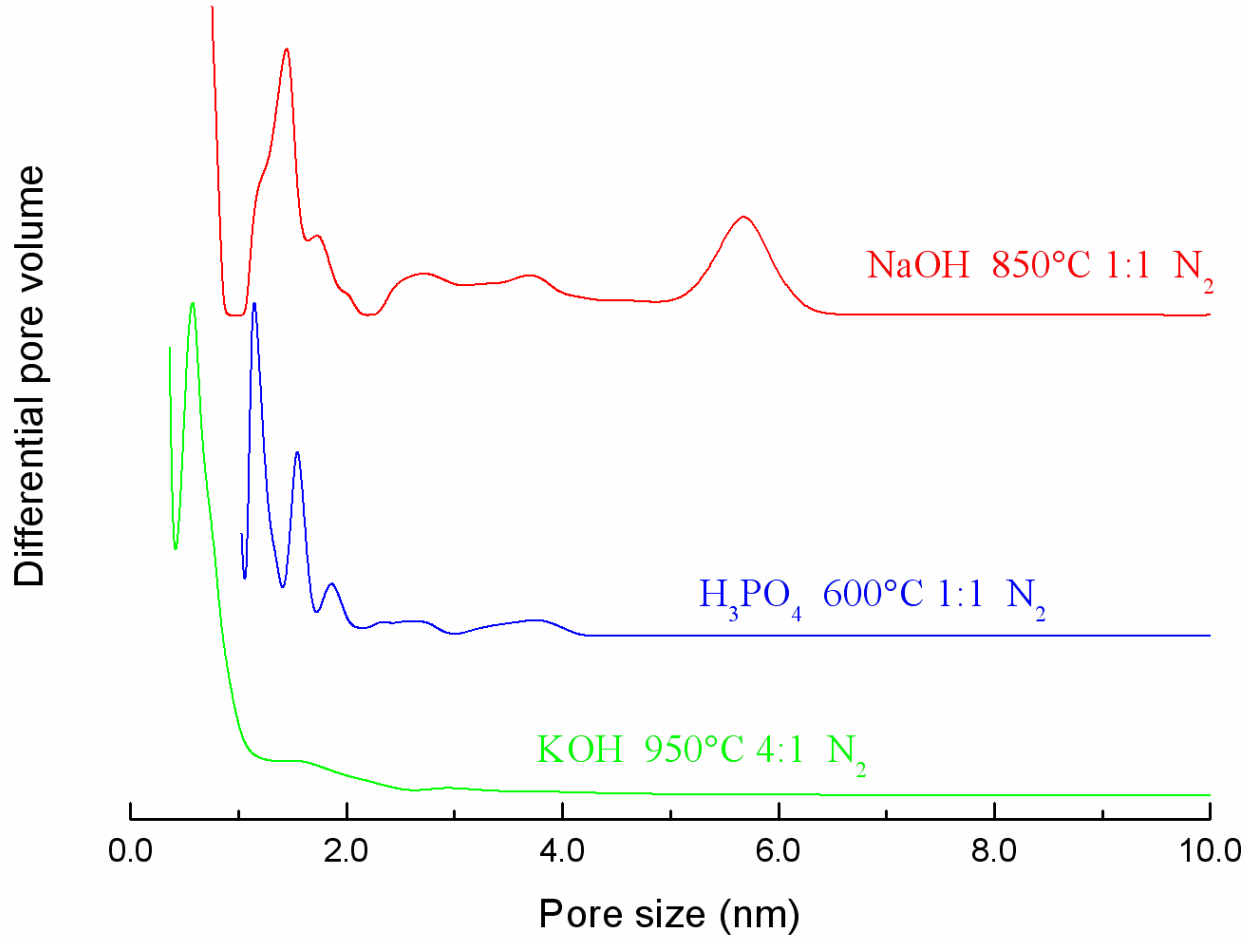
Textural analysis

N_2 sorption isotherms (77 K) – AC from testa of oil seeds



Textural analysis

Pore size distributions (NLDFT) – AC from testa of oil seeds

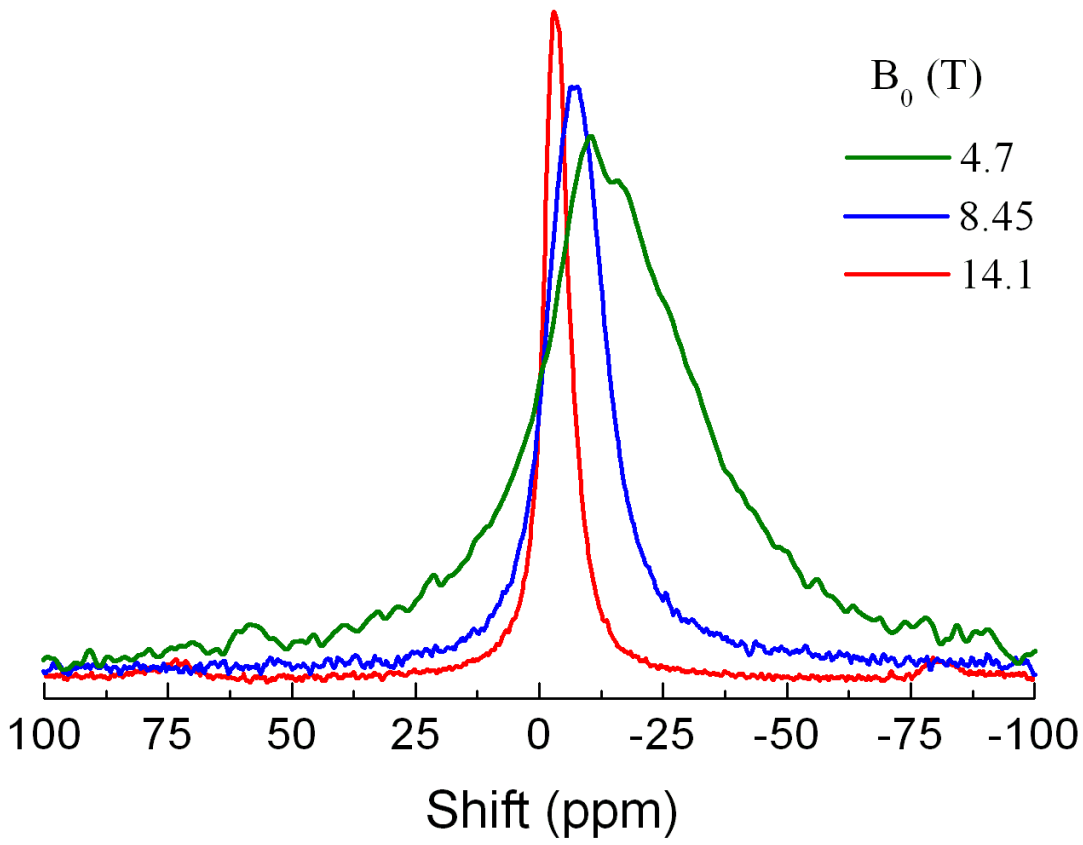


^{23}Na NMR results

NaOH activated carbons

(rice hulls)

- Single-pulse experiments.
- MAS at 12 kHz.
- Probes: 4 mm.

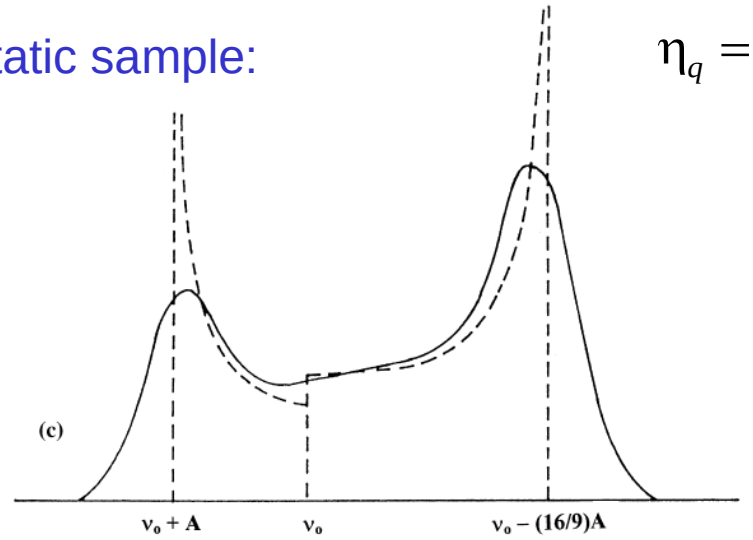


Quadrupole effects in MAS NMR spectra

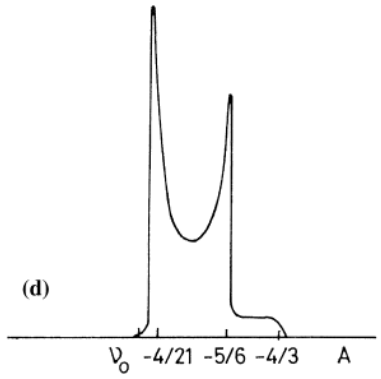
Powder patterns – half-integer spin nuclei:

Static sample:

$\eta_q = 0$



MAS:



2nd order – central transition:

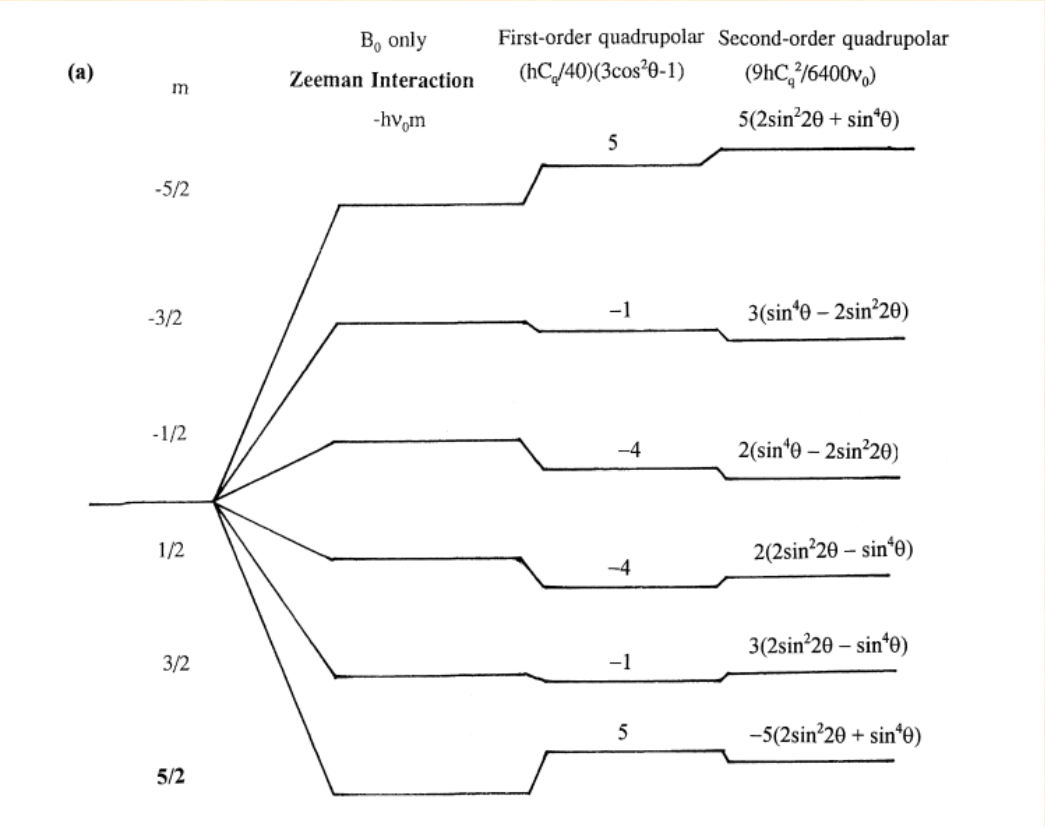
$$\nu_q = \frac{3e^2qQ}{2I(2I-1)h}$$

$$A = \left[I(I+1) - 3/4\right]\frac{\nu_q^{\,2}}{\nu_0}$$

Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

Quadrupole effects in MAS NMR spectra

Energy levels: Zeeman interaction + electric quadrupole coupling (*perturbation*):



$$\nu_m^{(1)} = (3C_q/4I(2I-1))(3\cos^2\theta - 1)(m_z - 1/2)$$

$$\nu_m^{(2)} = (-9C_q^2/64\nu_o I^2(2I-1)^2)(a - 3/4)(1-\cos^2\theta) \times (9\cos^2\theta - 1) \quad (4)$$

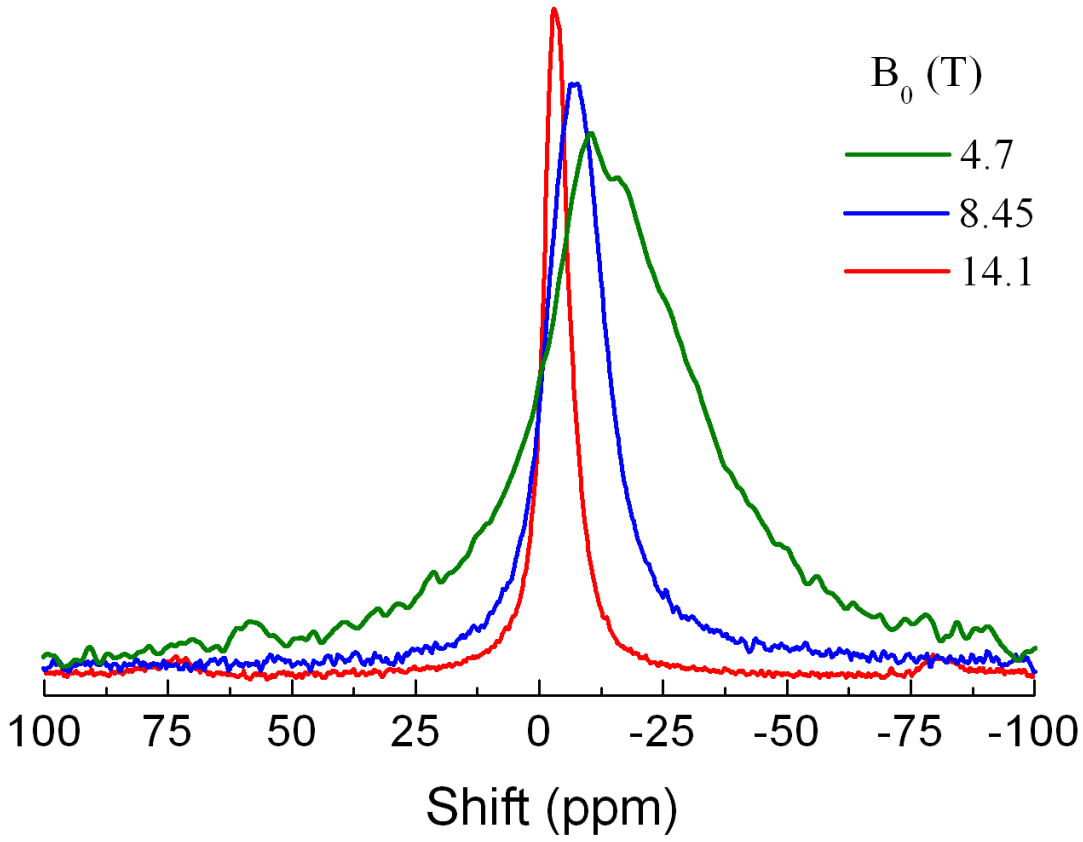
Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

^{23}Na NMR results

NaOH activated carbons

(rice hulls)

- Single-pulse experiments.
- MAS at 12 kHz.
- Probes: 4 mm.



Disordered materials: no quadrupolar features directly observed.

Quadrupole effects in MAS NMR spectra

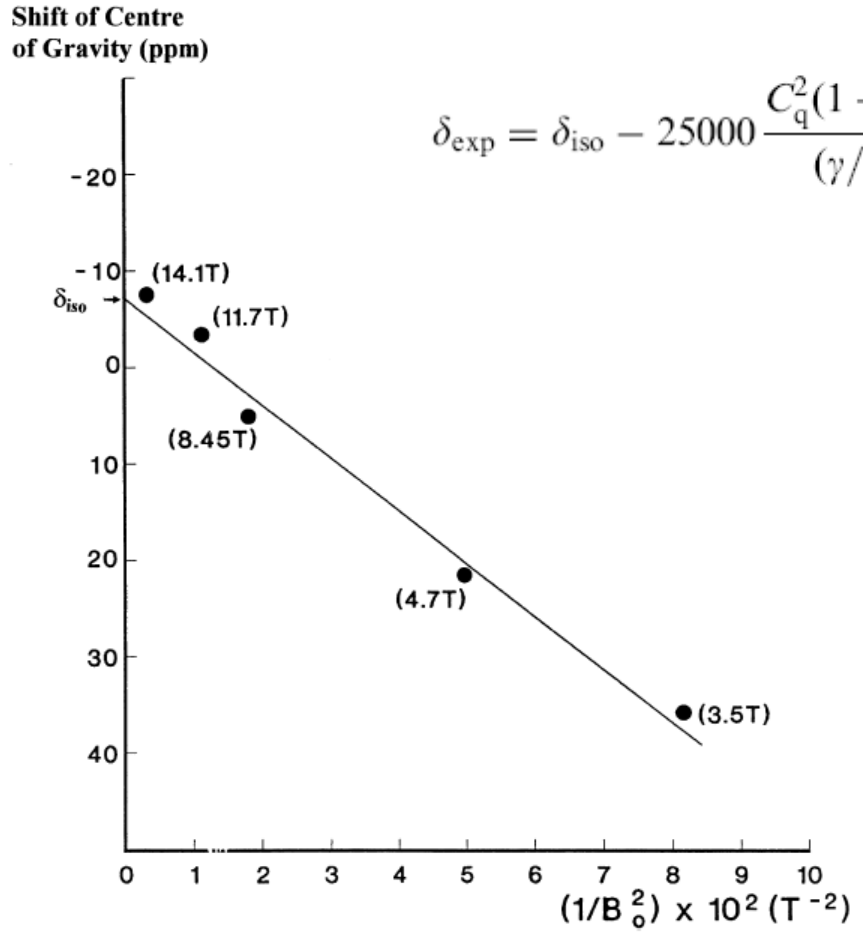


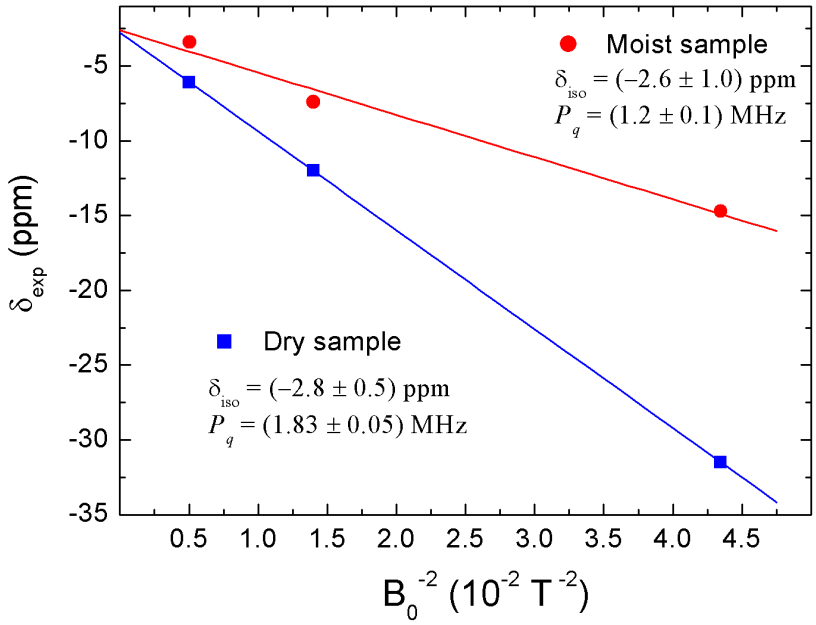
Fig. 13. Position of the centre of gravity of the ^{27}Al MAS NMR spectra from kaolinite ($Al_2Si_2O_5(OH)_4$) plotted against B_o^{-2}.

Smith & van Eck, *Prog. Nucl. Magn. Reson. Spectr.* 1999;34:159-201

^{23}Na NMR results

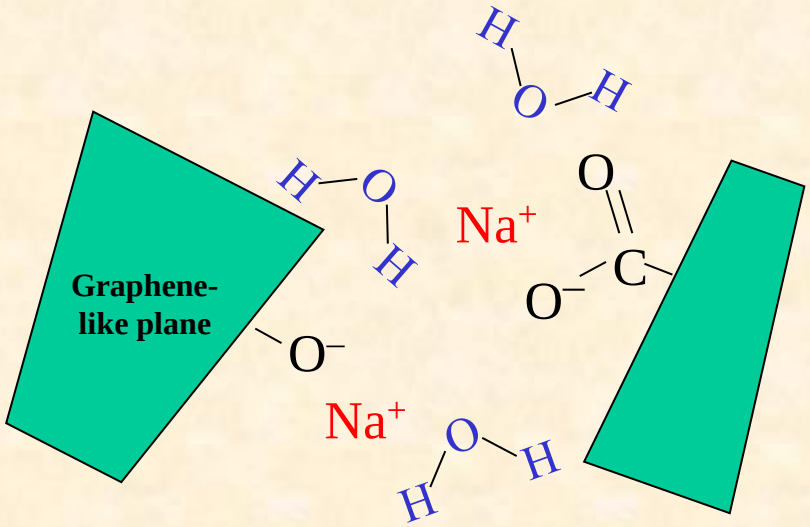
NaOH activated carbons

(rice hulls)

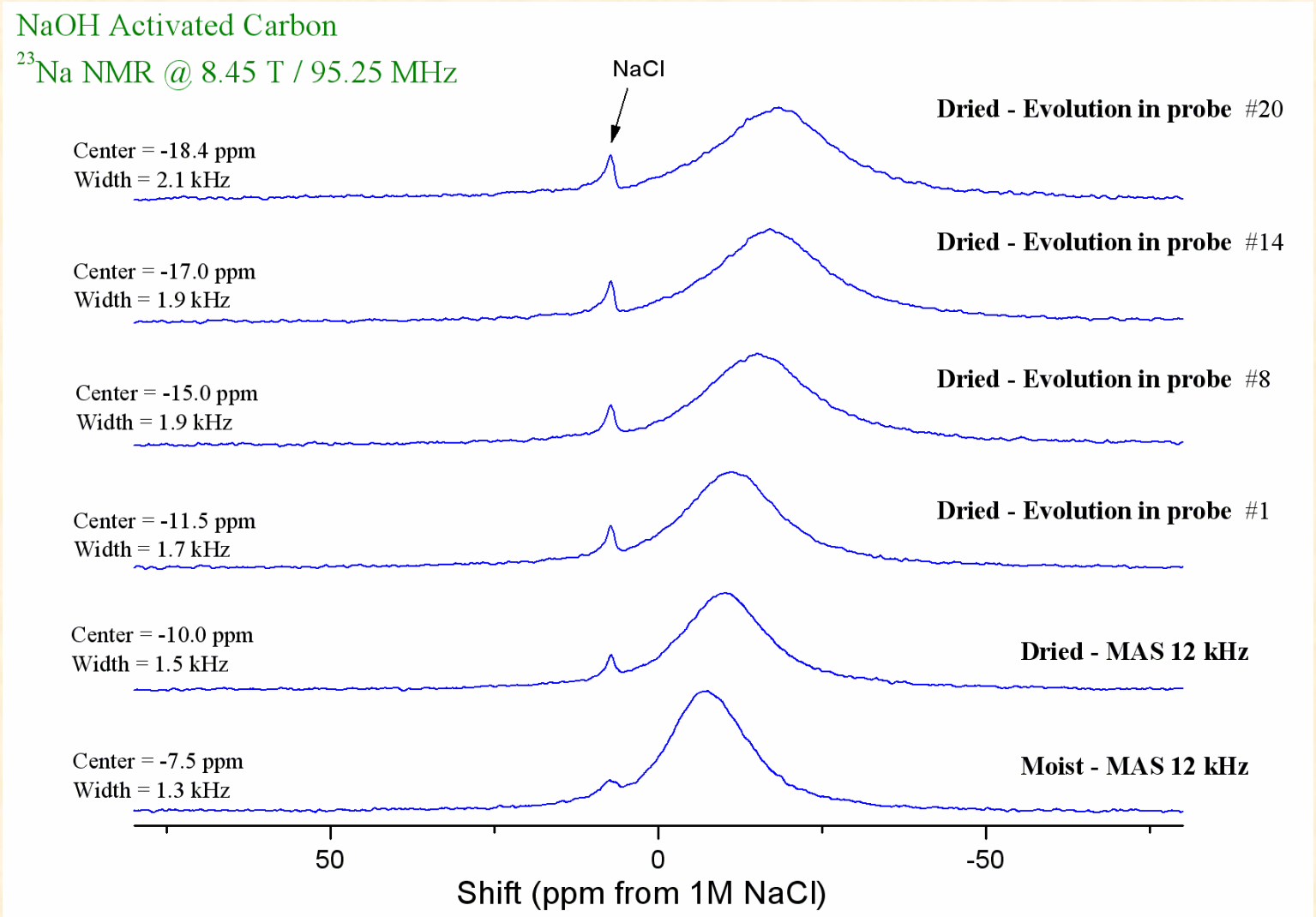


Freitas et al., *SSNMR* 2007;32:109

- ✓ Isotropic chemical shifts are indicative of the occurrence of oxygenated Na groups.
- ✓ Possible existence of surface groups containing Na-O-C bonds at the edges of aromatic lamellae.
- ✓ Strong effect of hydration on quadrupolar coupling.



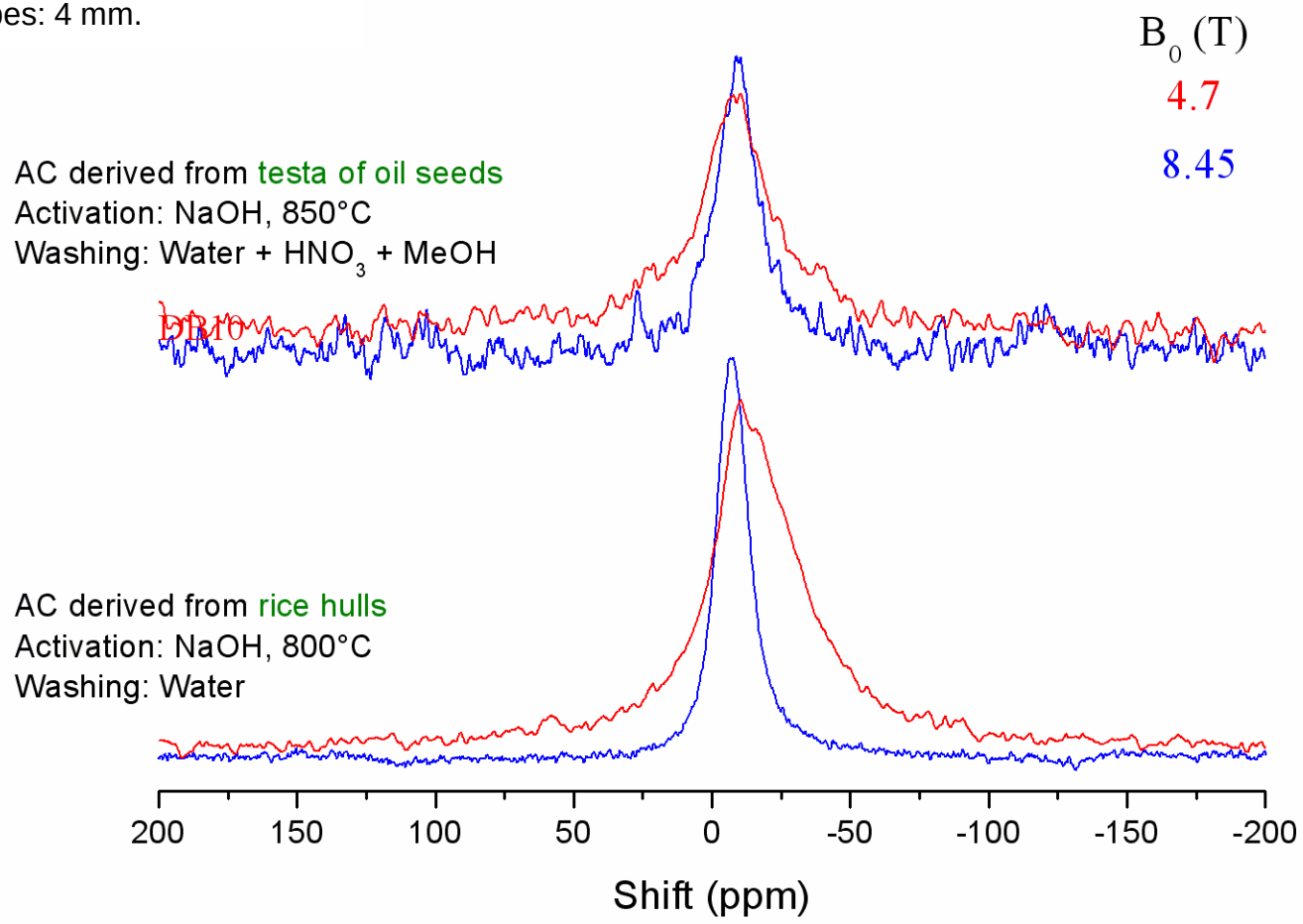
^{23}Na NMR results



Spectra change as a function of experiment time – effects of drying.

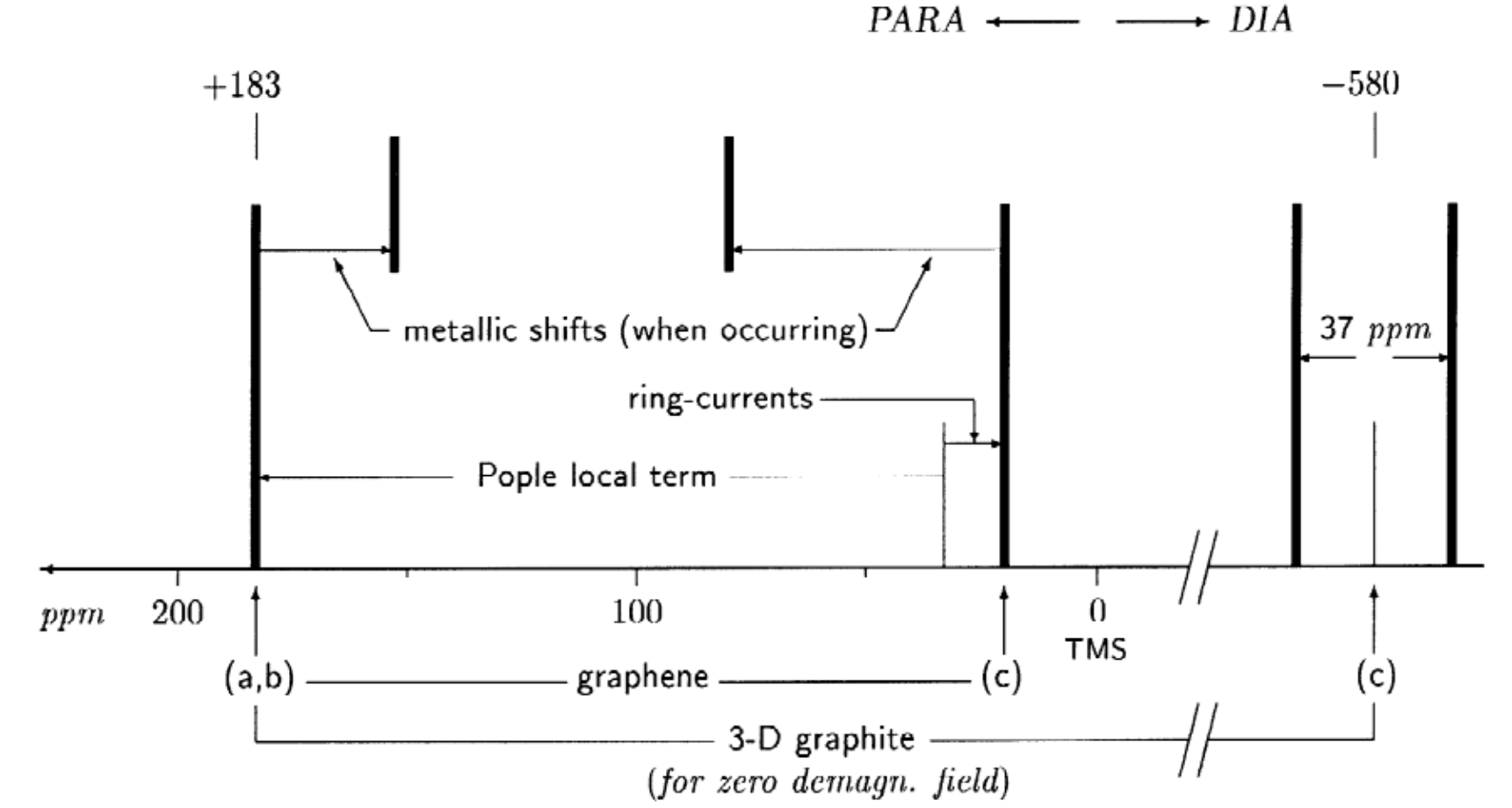
^{23}Na NMR results

- Single-pulse experiments.
- MAS: 10 kHz.
- Probes: 4 mm.



^{13}C NMR spectroscopy

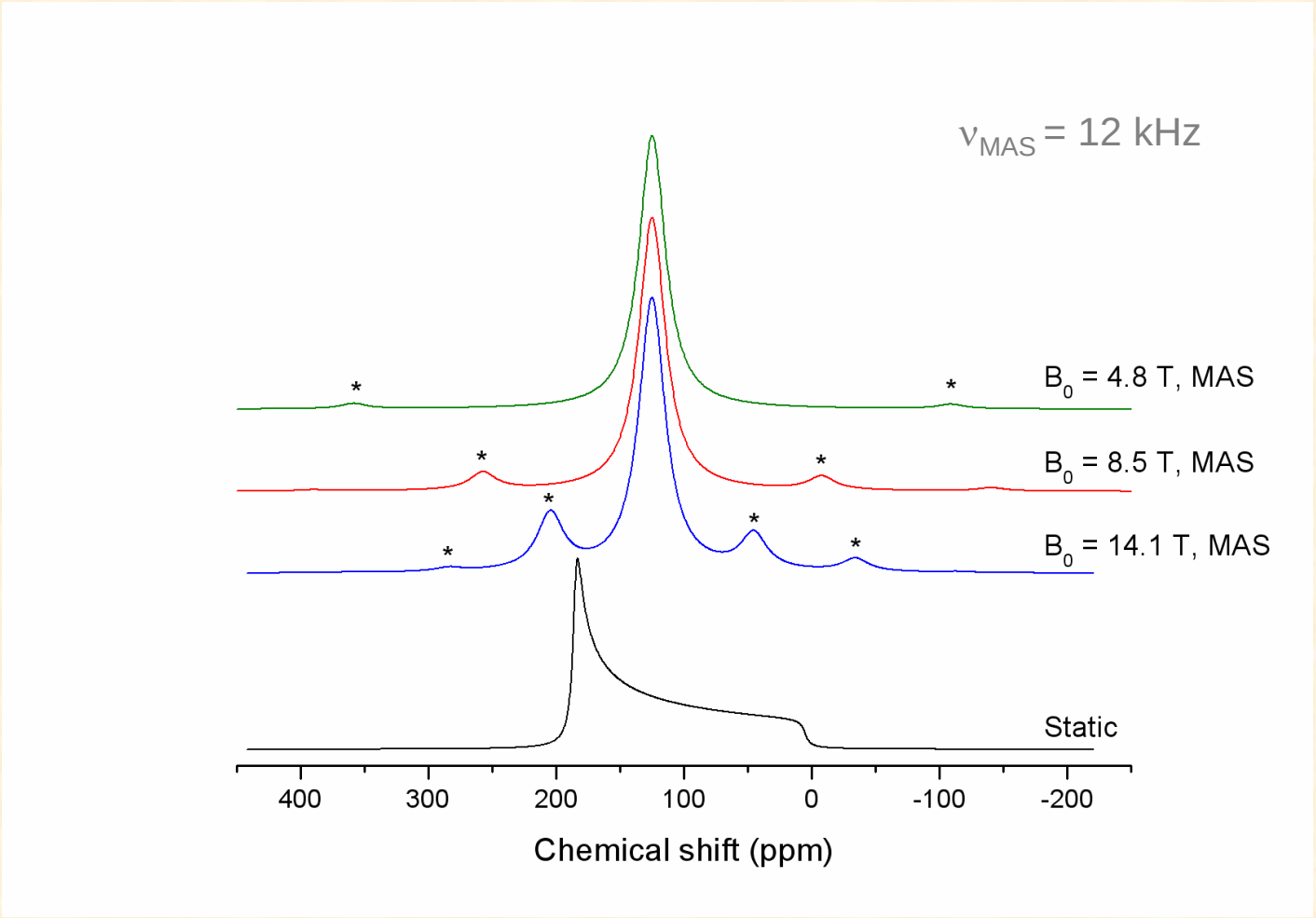
Overview of ^{13}C NMR shifts in graphene, graphite and related compounds:



Goze-Bac et al., *Carbon* 2002;40:1825

^{13}C NMR spectroscopy

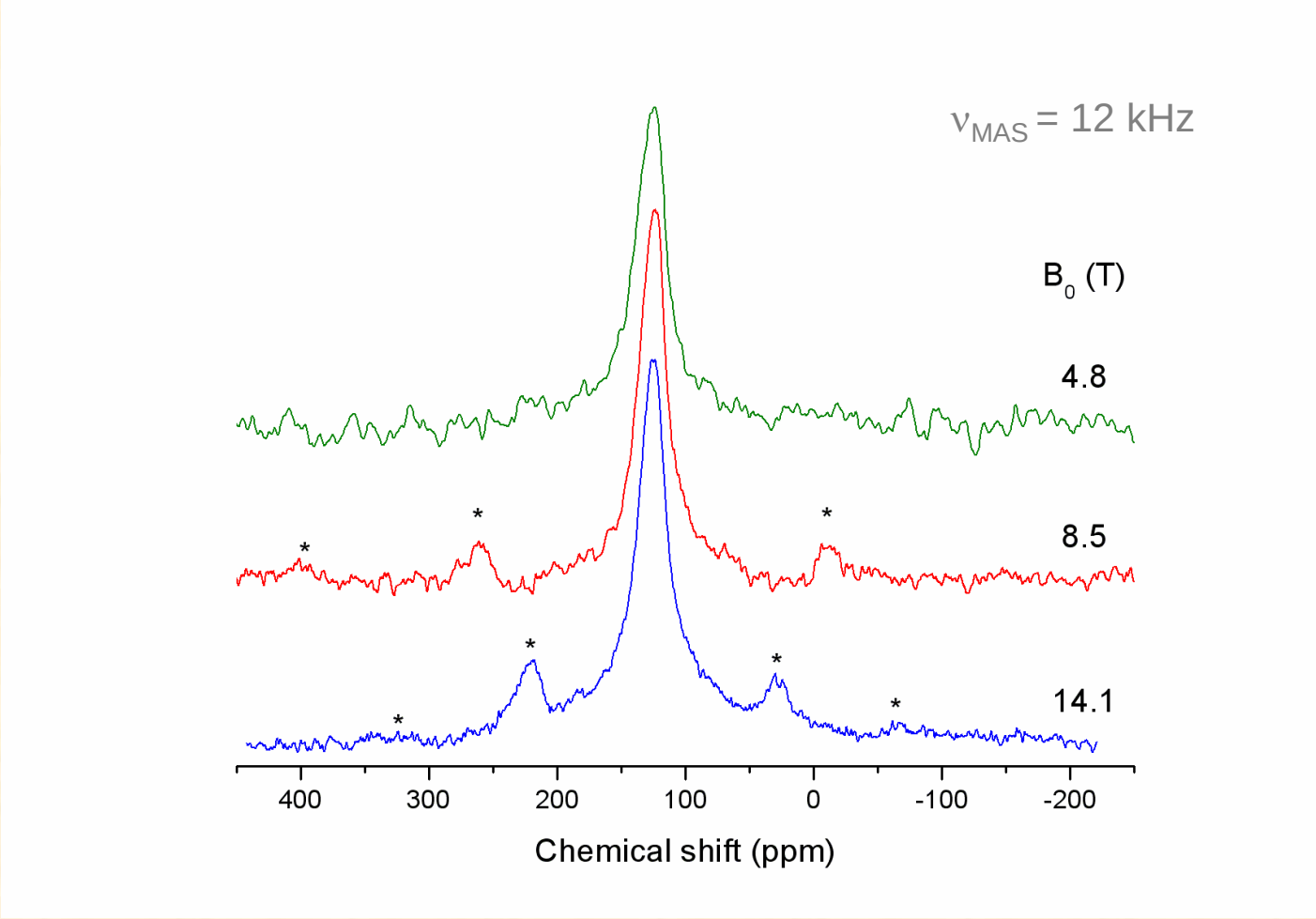
Simulated ^{13}C NMR spectra of a graphene-like material – CSA effects:



CSA: *Chemical Shift Anisotropy*

^{13}C NMR spectroscopy

Spectra recorded for carbons at different magnetic field strengths:



^{13}C NMR spectroscopy

CSA effects for different magnetic field strengths:

B_0 (T)	^{1}H NMR frequency (MHz)	^{13}C NMR frequency (MHz)	Δf_{CSA} (kHz)
2.35	100	25.2	5
4.70	200	50.3	10
7.05	300	75.4	15
9.39	400	100.6	20
11.74	500	125.8	25
14.09	600	150.9	30
16.44	700	176.1	35
18.79	800	201.2	40
21.14	900	226.4	45

Effect of heat-treatment temperature

^{13}C NMR spectra of heat-treated carbon materials:

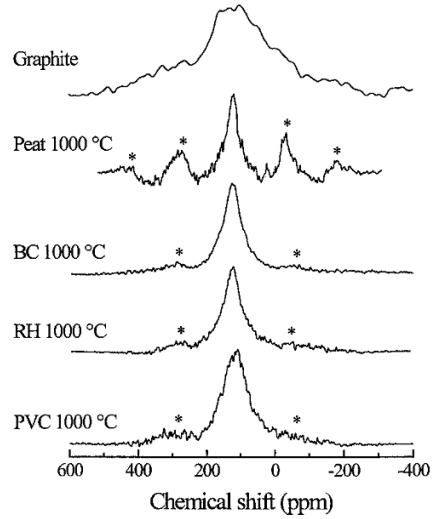


FIG. 1. ^{13}C MAS NMR spectra of polycrystalline graphite and heat-treated carbon samples (prepared from the various precursors at the indicated HTTs). Asterisks denote spinning sidebands.

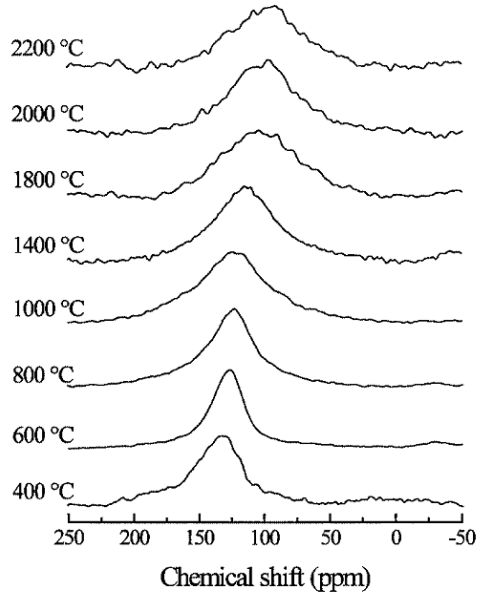
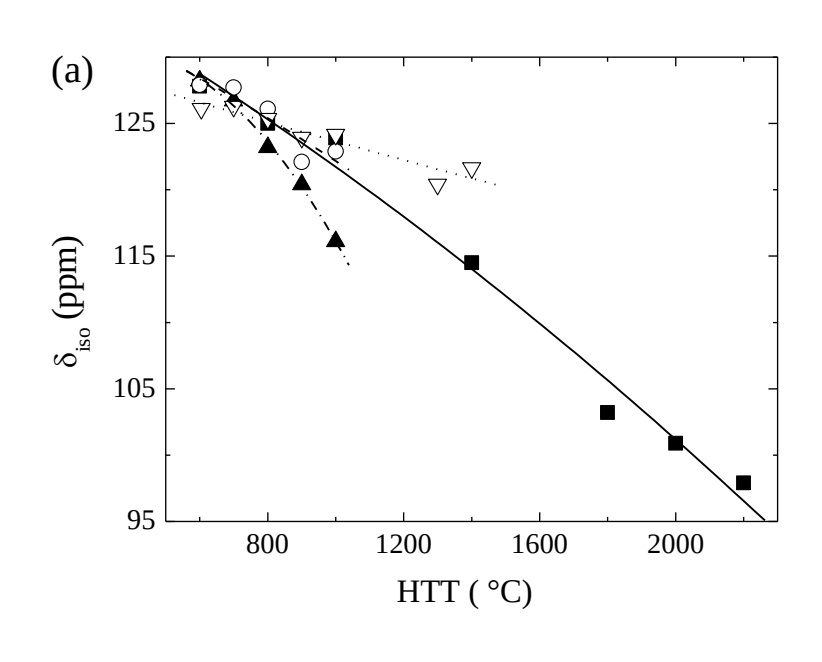


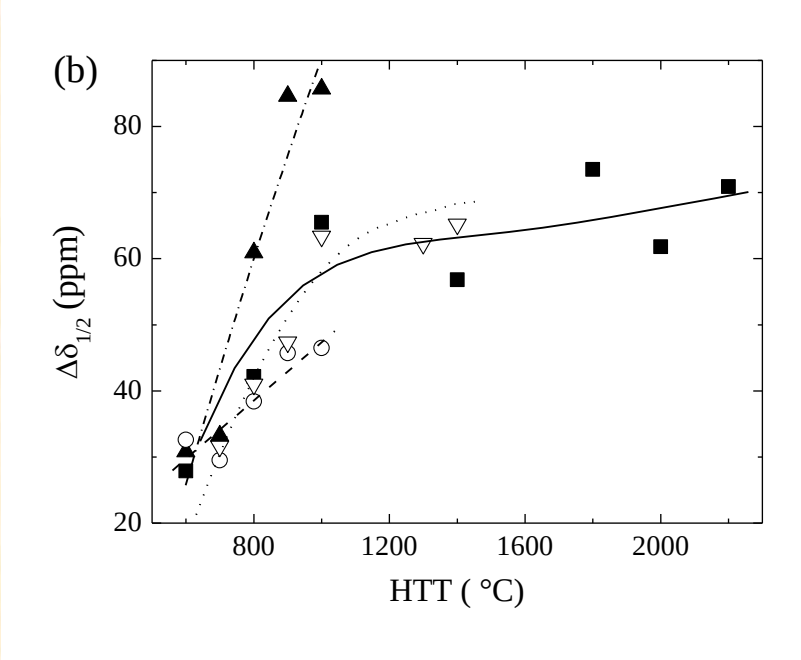
FIG. 2. ^{13}C MAS NMR spectra of BC samples prepared at the indicated HTTs.

Freitas et al., *SSNMR* 2001;20:61

Effect of heat-treatment temperature

^{13}C NMR spectra of heat-treated carbon materials:

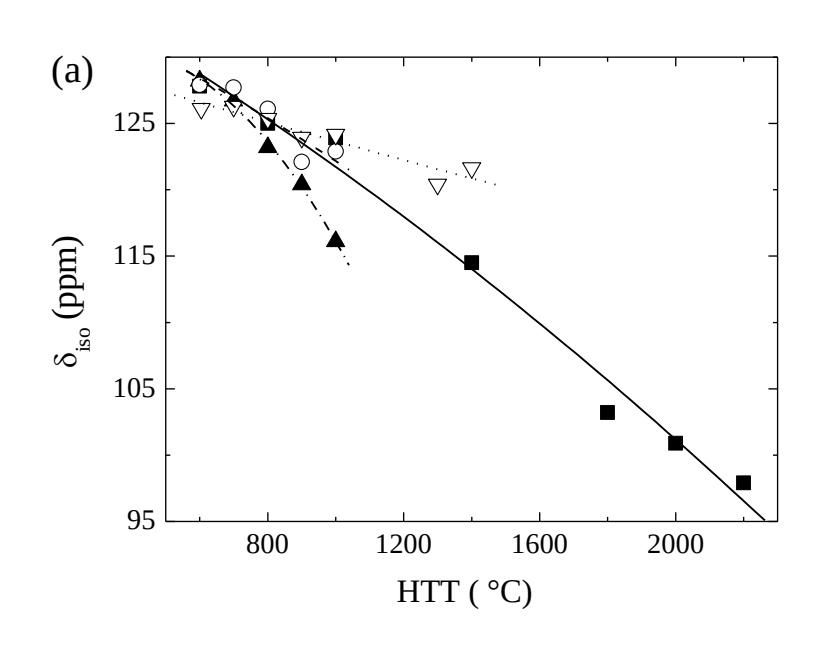


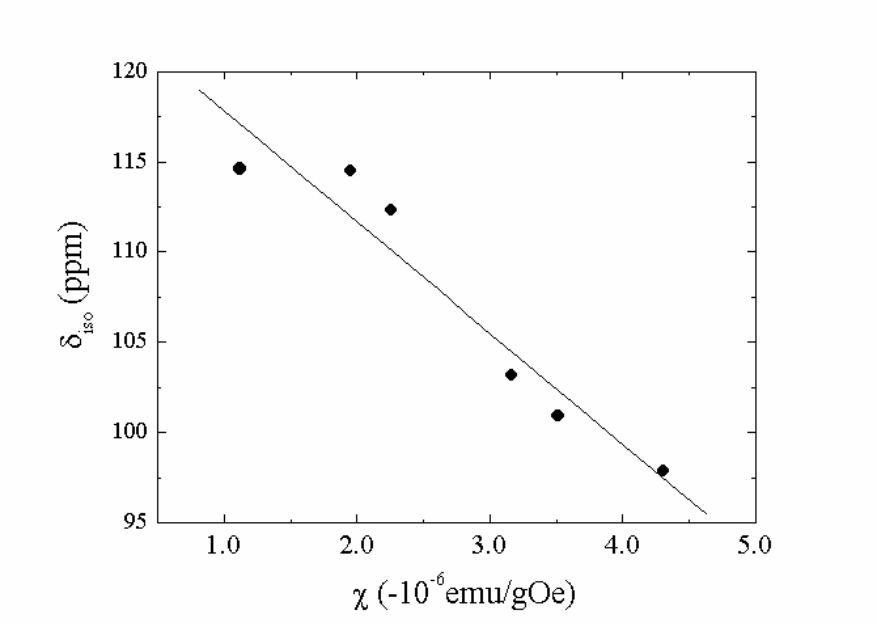


Freitas et al., *SSNMR* 2001;20:61

Effect of heat-treatment temperature

^{13}C NMR spectra of heat-treated carbon materials:





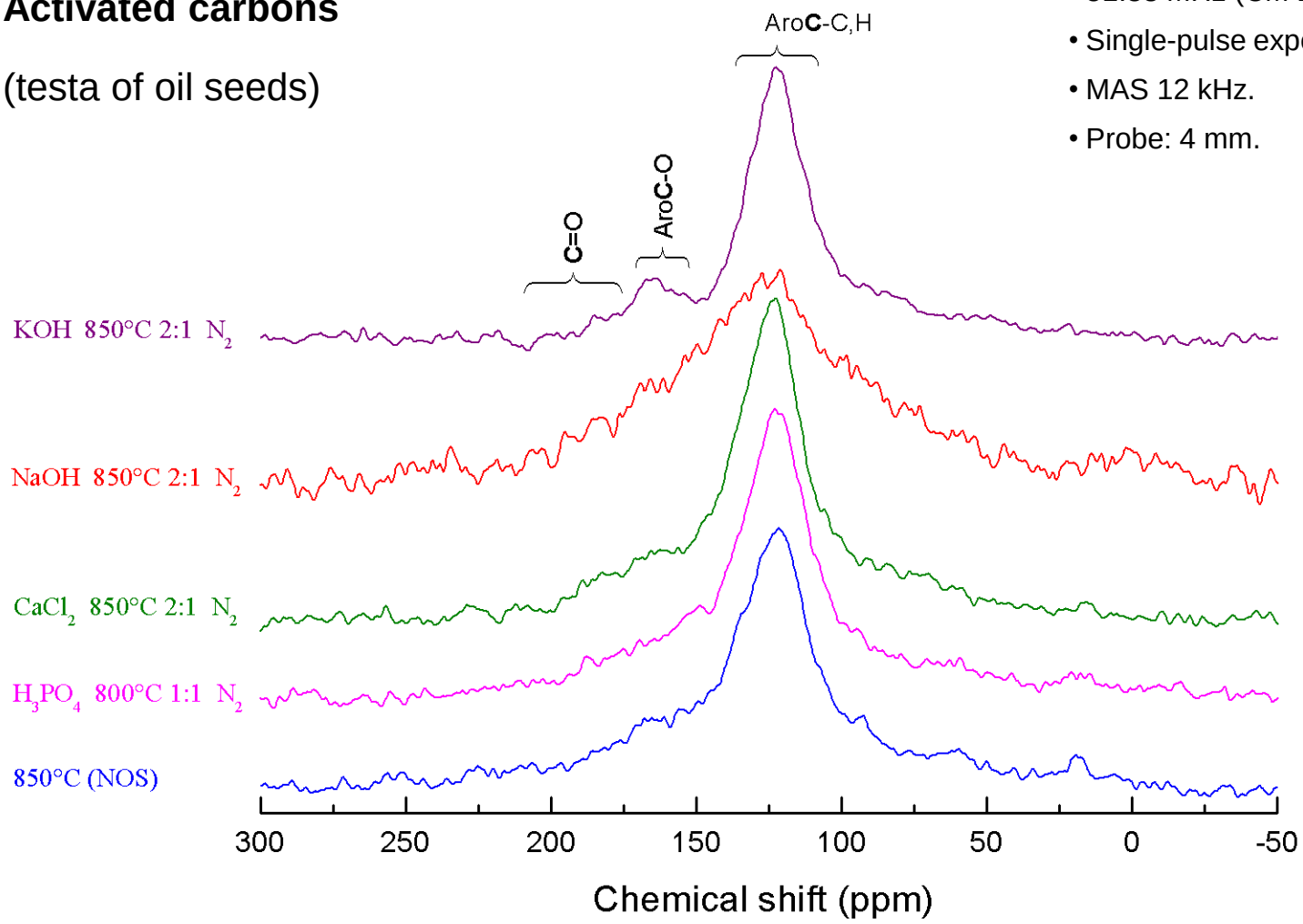
Freitas et al., *SSNMR* 2001;20:61

^{13}C NMR results

Activated carbons

(testa of oil seeds)

- 51.38 MHz (CM 200).
- Single-pulse experiments.
- MAS 12 kHz.
- Probe: 4 mm.

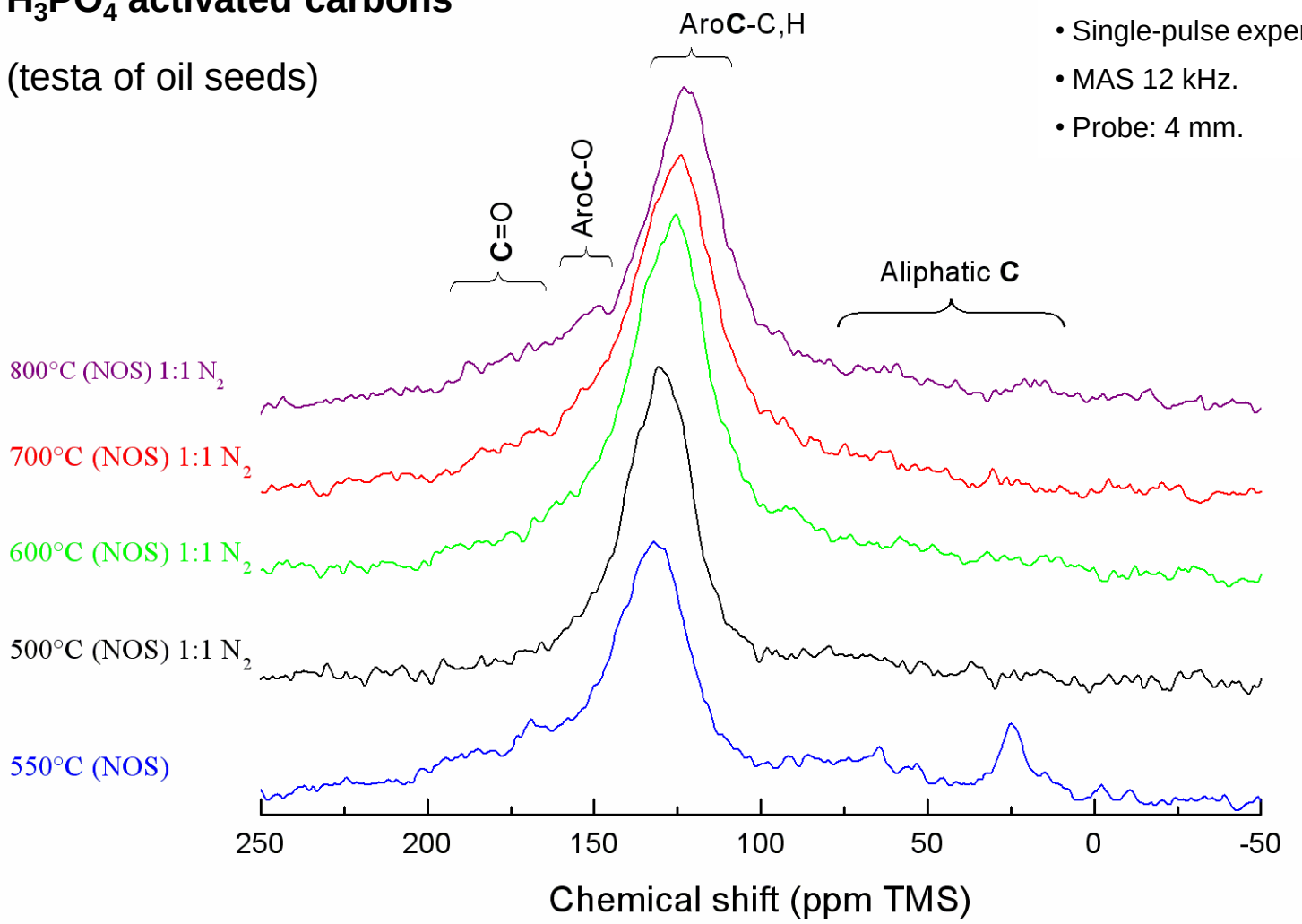


^{13}C NMR results

H_3PO_4 activated carbons

(testa of oil seeds)

- 51.38 MHz (CM 200).
- Single-pulse experiments.
- MAS 12 kHz.
- Probe: 4 mm.

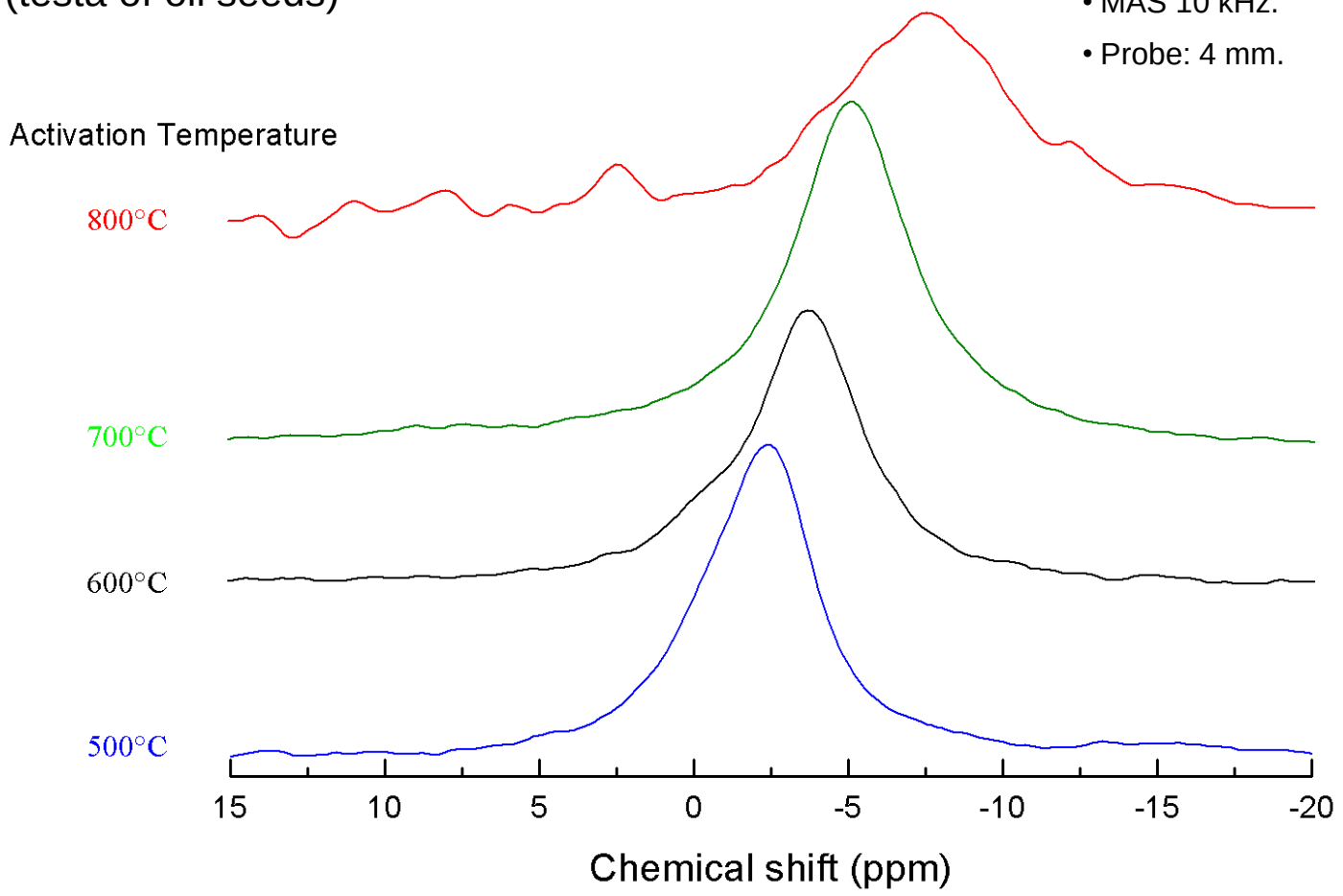


^{31}P NMR results

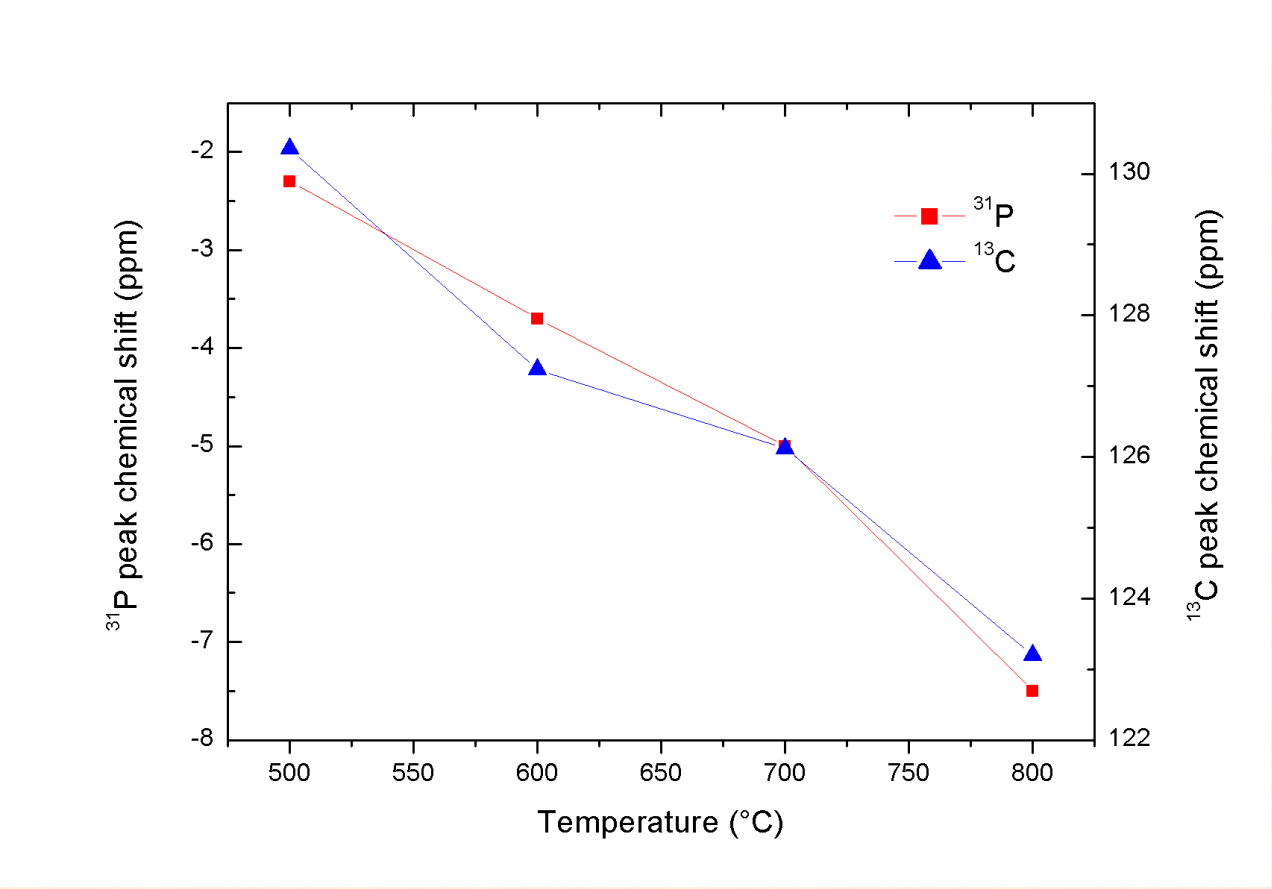
H_3PO_4 activated carbons

(testa of oil seeds)

- 145.77 MHz (CM 360).
- Single-pulse experiments.
- MAS 10 kHz.
- Probe: 4 mm.



Effect of heat-treatment temperature



Increase in the locally anisotropic diamagnetic susceptibility associated with the graphene-like planes.

Conclusions

- Solid-state NMR was used in conjunction with other characterization techniques to study a series of activated carbons prepared from different chemical activating agents.
- The predominantly aromatic nature of all activated materials was clearly established; oxygenated functional groups were detected especially for the alkali-activated carbons.
- The presence of Na^+ ions was observed by ^{23}Na NMR experiments conducted at multiple magnetic fields, with the symmetry around these sites being largely affected by the hydration level.
- For samples prepared at different temperatures, the chemical shift of the aromatic resonance in ^{13}C NMR spectra showed a trend of reduction with the increase in the activation temperature, caused by the increase in the diamagnetic susceptibility of the graphene-like planes in the activated carbons.
- The same trend was also observed in ^{31}P NMR spectra, indicating the close intimacy between the phosphorous species and the aromatic planes in the nanoporous carbons.

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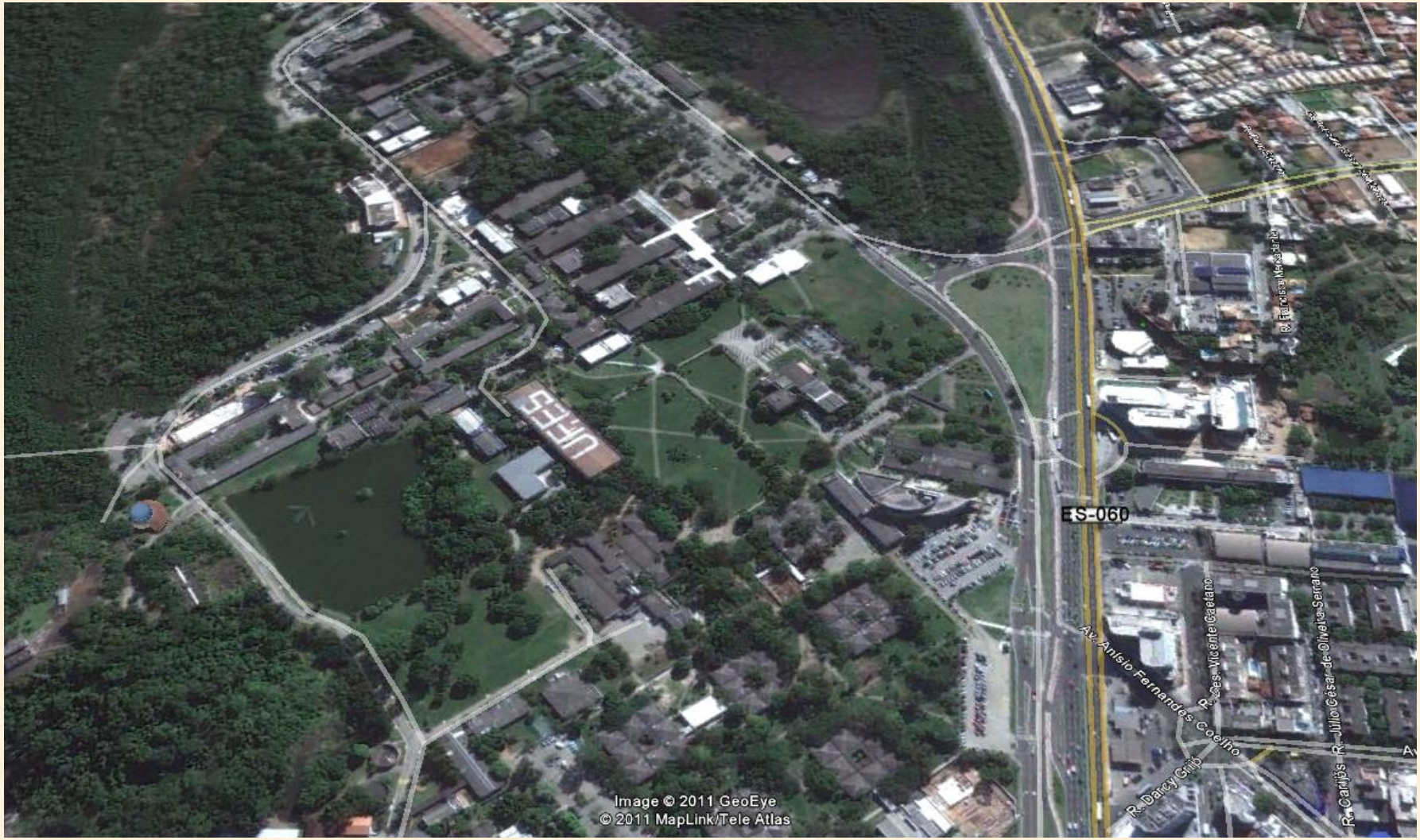
- Federal University of Espírito Santo (Brazil) – leave.
- CNPq, FAPES and CAPES (Brazil) – funding.

Aerial view of UFES:



Aerial view of UFES:


Welcome to Vitória (anytime...)