Aplicações de RMN no estado sólido para o estudo de materiais de carbono: de biocarvões ao grafeno

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Sumário

- **Introdução aos materiais de carbono.**
  - **Estrutura, propriedades físicas, …**
- **Estudos via RMN no estado sólido.**
  - **RMN de ^{13}C.**
  - **Outros núcleos-sonda.**
- **Estado da arte – materiais e/ou métodos avançados.**
  - **Materiais carbonosos porosos.**
  - **Biocarvões.**
  - **Óxido de grafite, grafeno e materiais relacionados.**

Materiais de carbono sólidos

- Formas cristalinas macroscópicas (“bulk”): grafite, diamante, fulerenos.
- Nanomateriais: nanotubos, grafeno, ...
- Outras formas: carbono amorfo, ...

100% C

- Carvões vegetais.
- Carvão mineral (hulha)
- Turfa, linhito, antracito.
- Coque, piche.
- “Carbon blacks”.
- Fuligem.
- Fibras de carbono.
- (...)

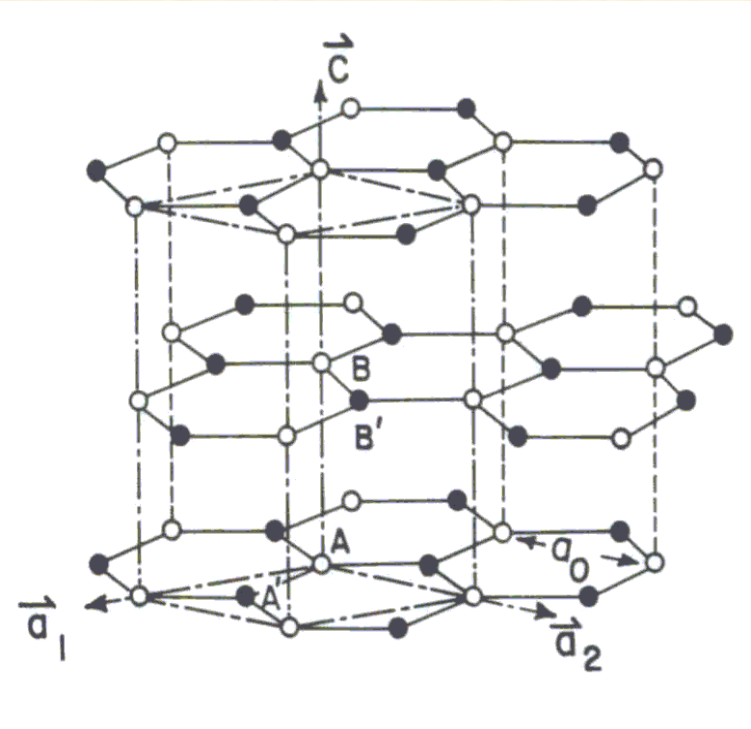
C *(majoritário)*

H, N, S, O, ...

Algumas diferentes formas de carbono

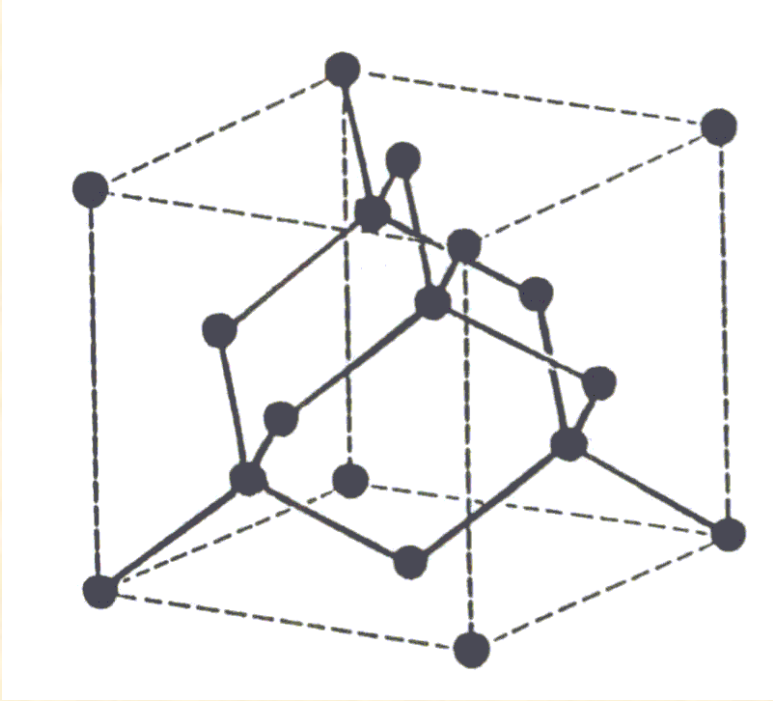
Grafite:

✓ Hibridização sp^2



Diamante:

✓ Hibridização sp^3



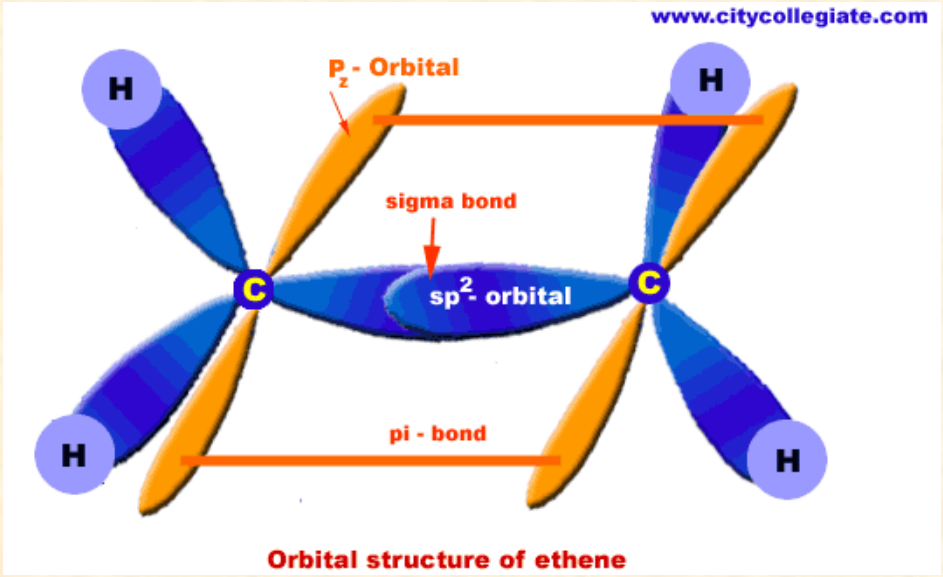
Algumas diferentes formas de carbono

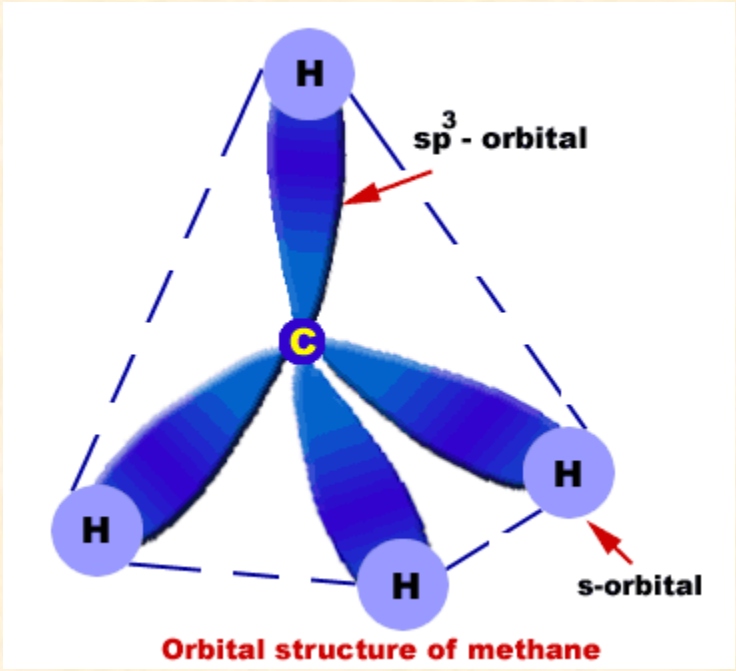
Grafite:

✓ Hibridização sp^2

Diamante:

✓ Hibridização sp^3





http://www.citycollegiate.com/hybridization1.htm

Grafeno e outras formas de carbono

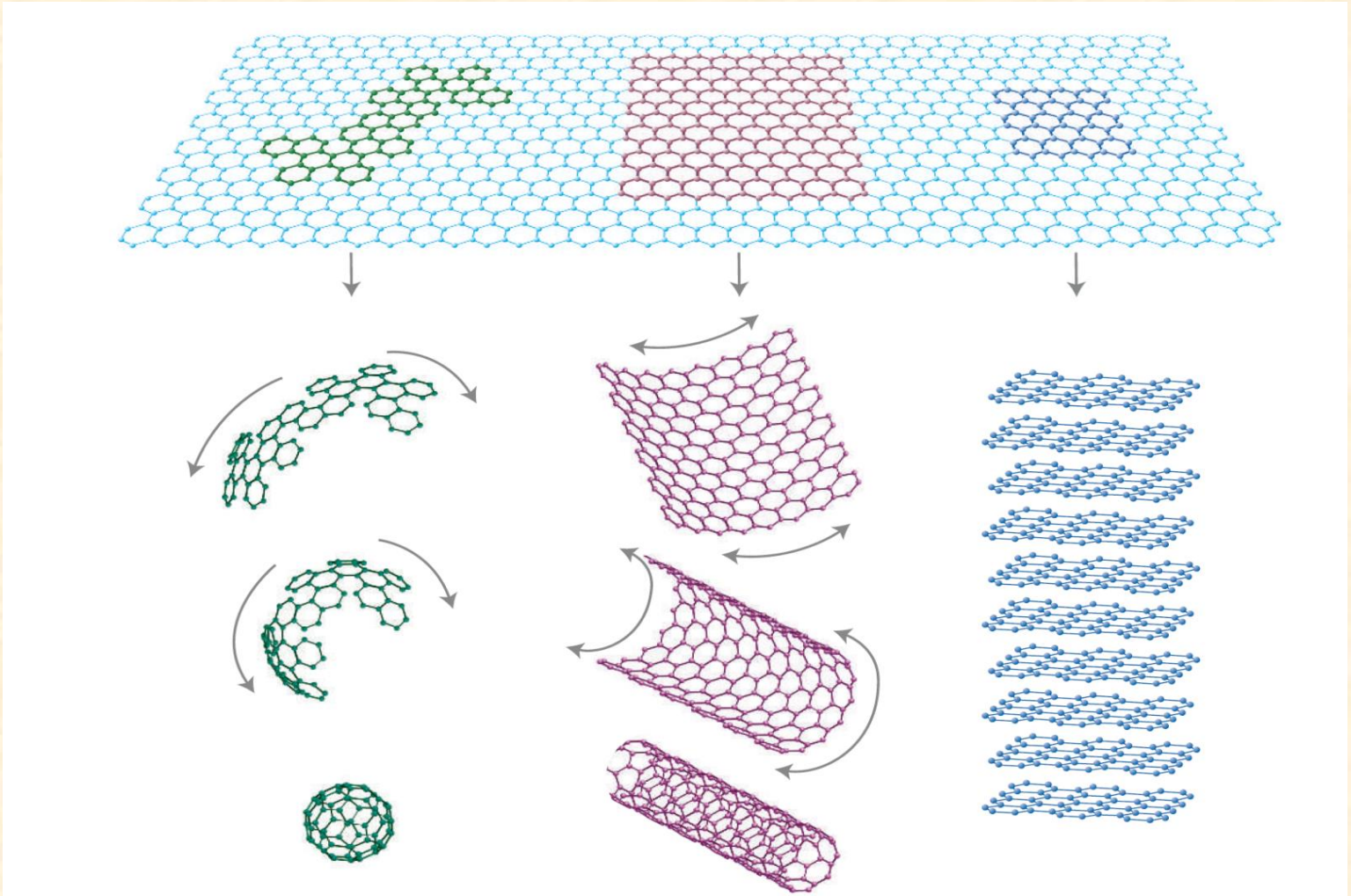


Figure 1 Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite.

Geim & Novoselov, *Nature Materials* 2007;6:183-191

Materiais carbonosos desordenados

- Sólidos porosos.
- Estrutura localmente semelhante ao grafite.
- Composição química principal: C, H, N, S, O.
- Fração menor de minerais (SiO_2, Fe_2O_3, ...).

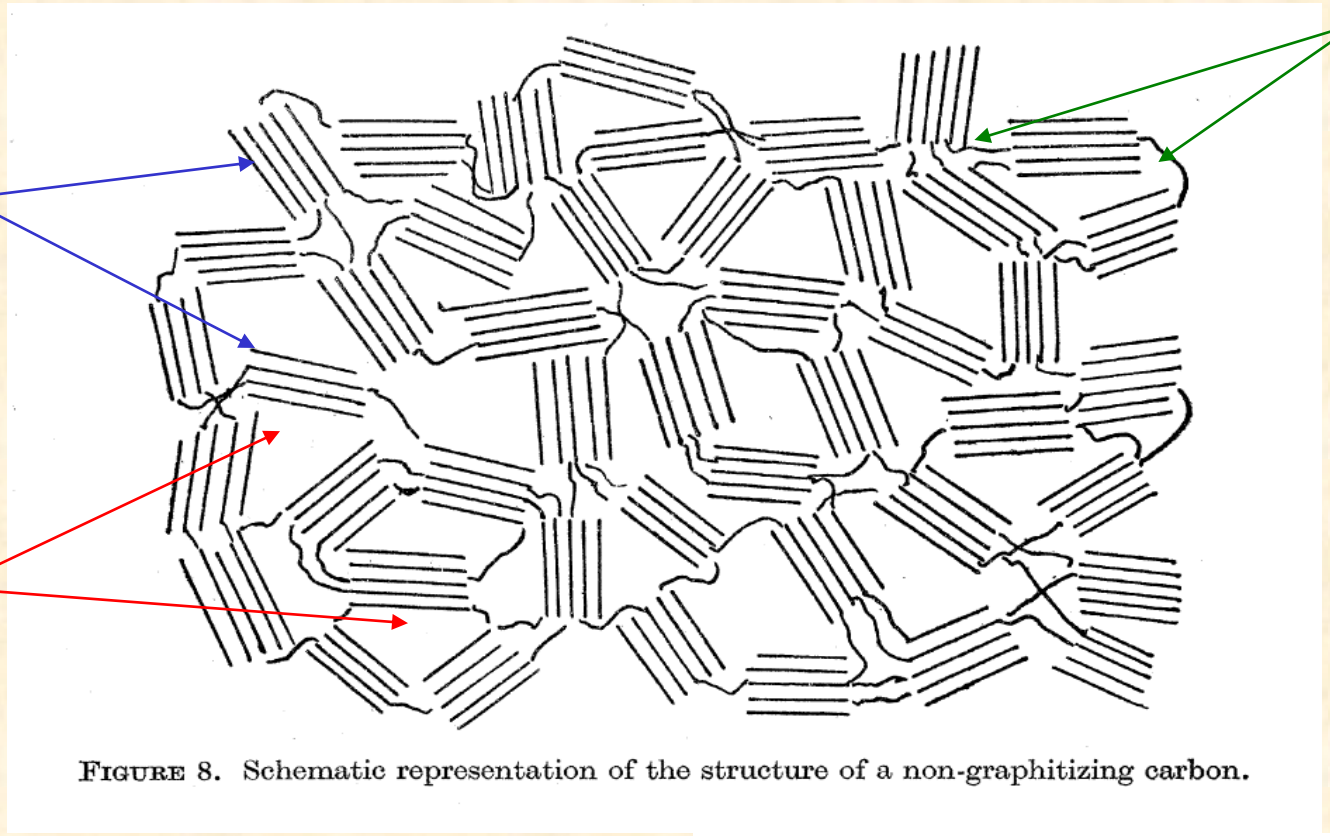


FIGURE 8. Schematic representation of the structure of a non-graphitizing carbon.

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

Materiais carbonosos desordenados

Estrutura turbostrática:

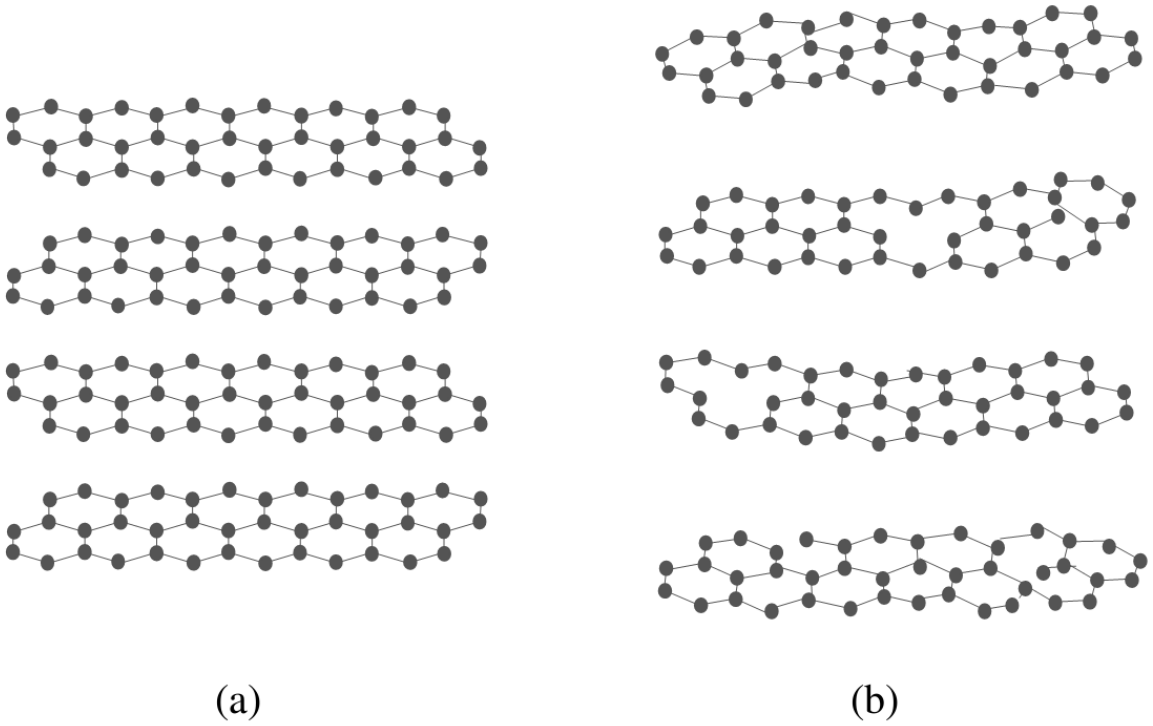
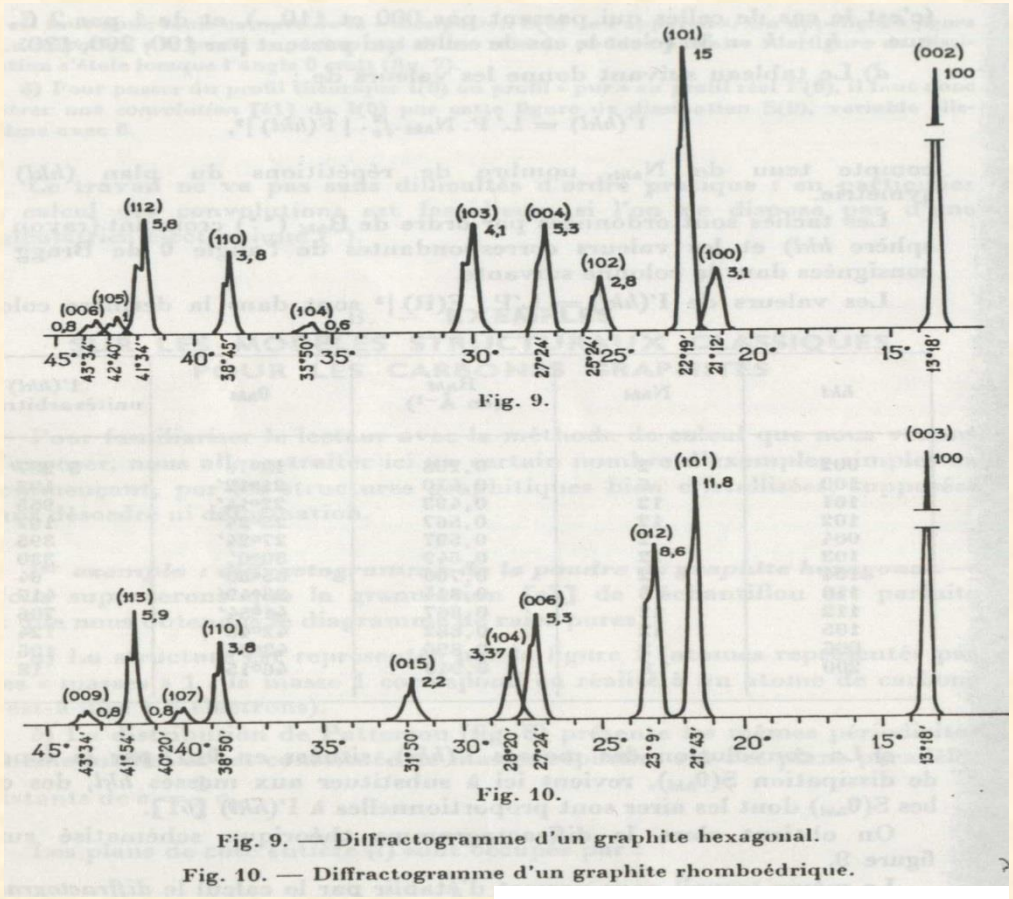


Figura 1.2: (a) Estrutura cristalina do grafite hexagonal. (b) Representação esquemática da estrutura turbostrática, ilustrando os defeitos internos aos planos, o reduzido grau de alinhamento e a distância interplanar aumentada em relação à estrutura do grafite.

Estrutura do grafite

Difração de raios X - grafite:



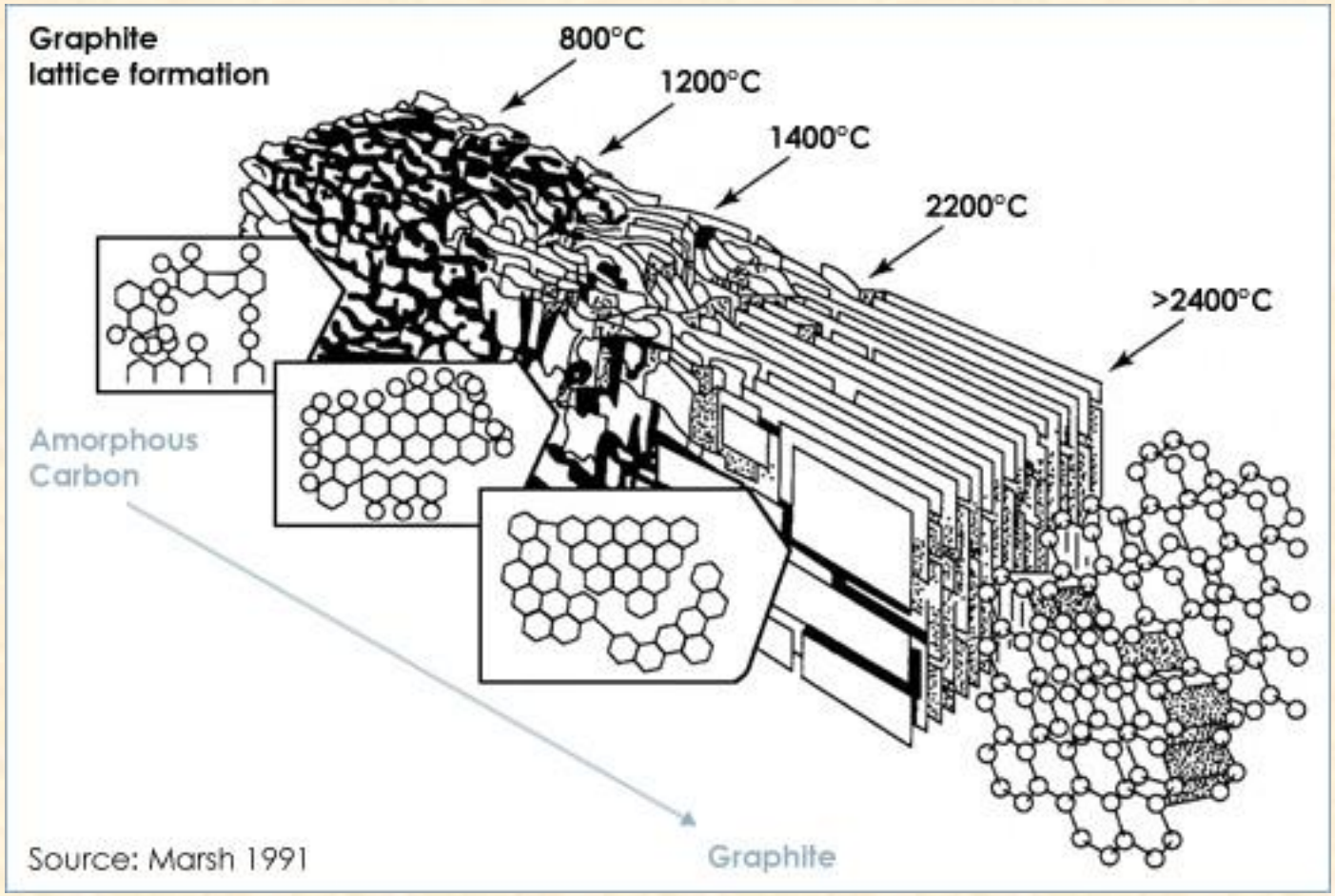
"*Les Carbones*", A. Pacault (org.)

Distância interplanar:

- ✓ Estrutura perfeita: d_{002} = 3,35 Å
- ✓ Estrutura turbostrática: d_{002} = 3,44 Å
- ✓ Materiais desordenados: $d_{002} \approx$ 3,7 Å
- ✓ Sensível ao grau de grafitização.

Processo de carbonização

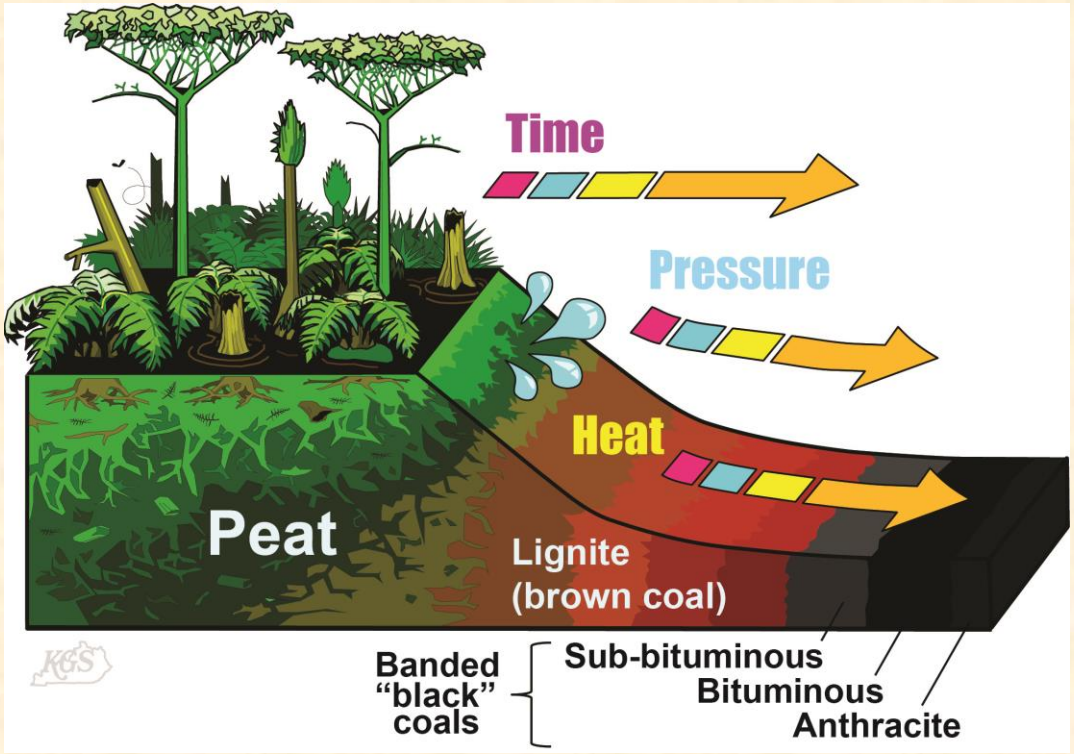
Tratamentos térmicos:

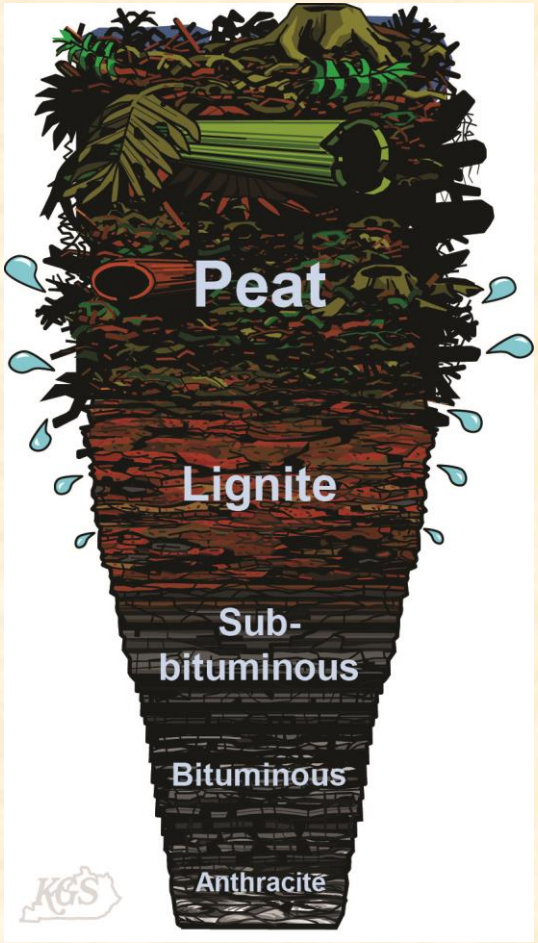


http://www.arrhenius.ucsd.edu/miakel/Miakel_B.html

Processo de carbonização

Formação de carvão mineral:





http://www.uky.edu/KGS/coal/coalform.htm

Materiais carbonosos desordenados

Materiais grafitizáveis e não-grafitizáveis – Modelo de Franklin:

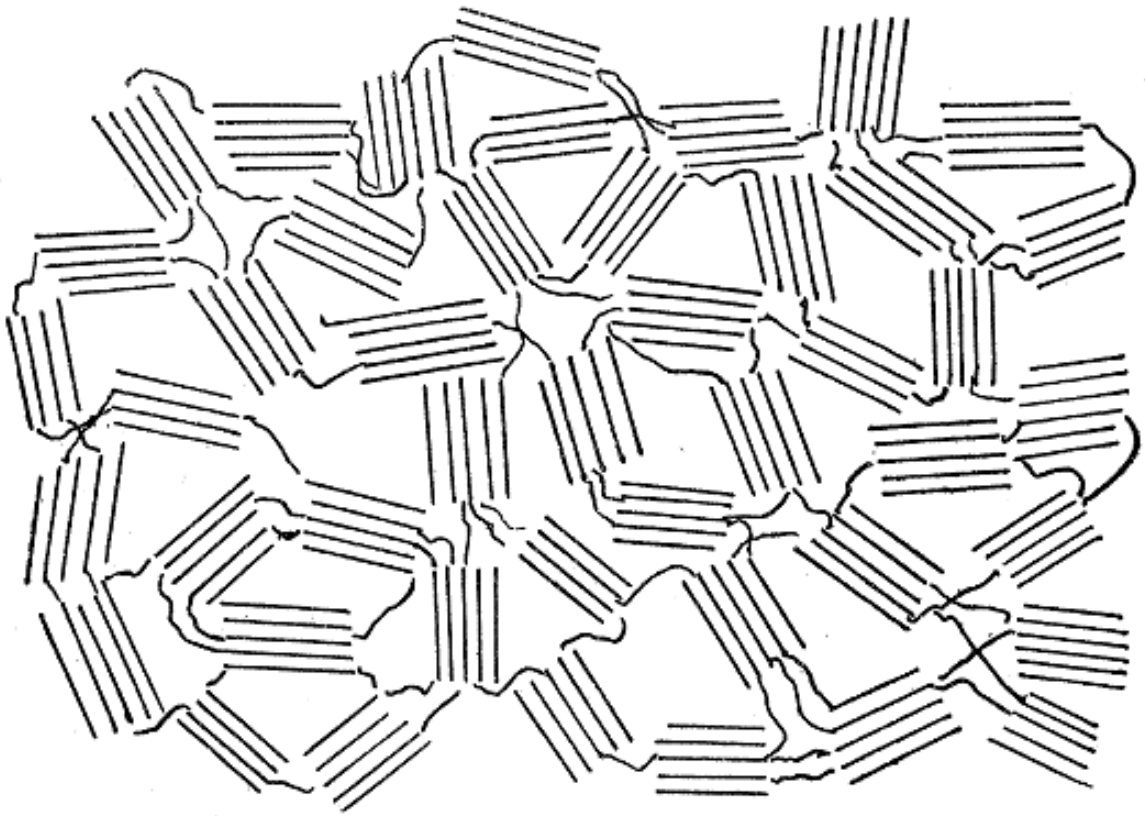


FIGURE 8. Schematic representation of the structure of a non-graphitizing carbon.

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

Materiais carbonosos desordenados

Materiais grafitizáveis e não-grafitizáveis – Modelo de Franklin:

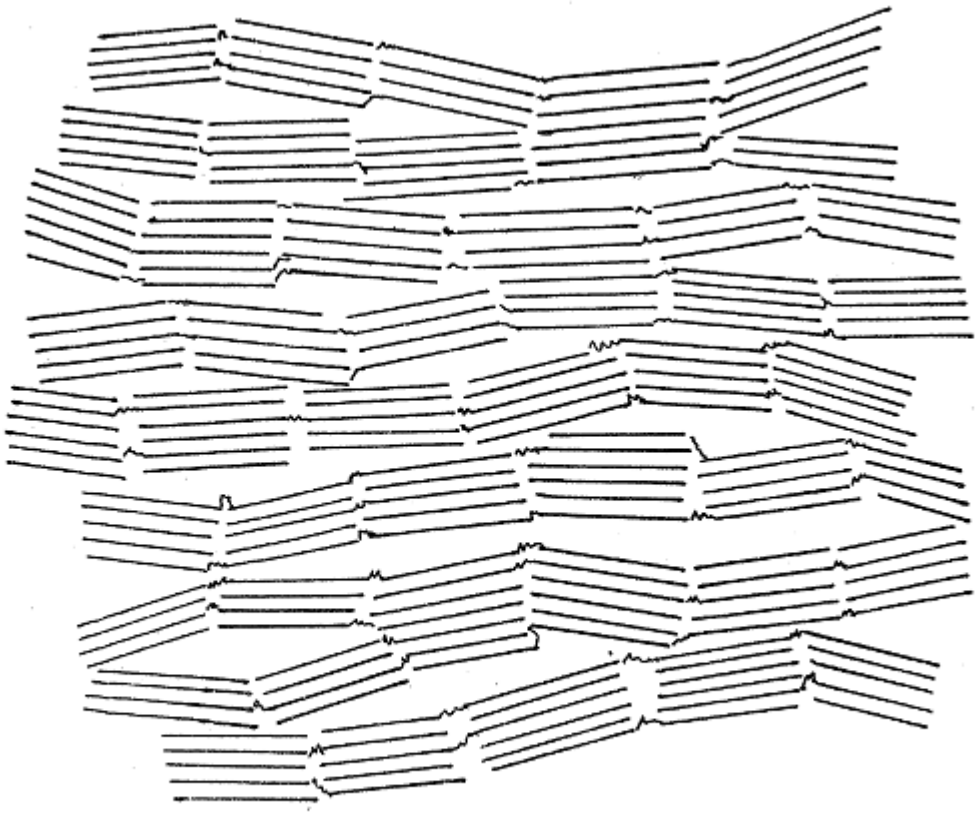


FIGURE 7. Schematic representation of the structure of a graphitizing (but non-graphitic) carbon.

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

Materiais carbonosos desordenados

Materiais grafitizáveis e não-grafitizáveis:

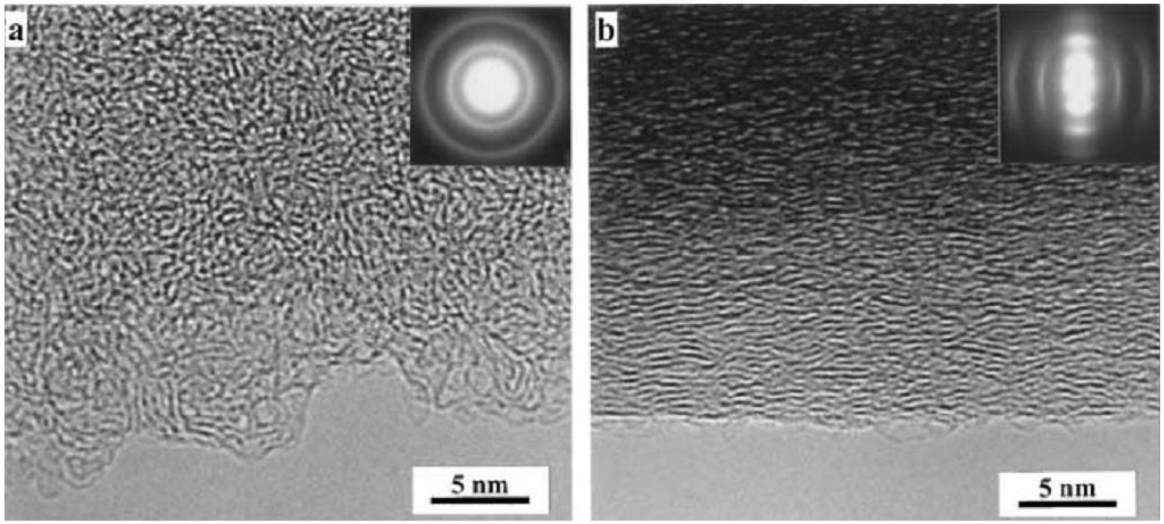


FIG. 7. (a) High resolution TEM image of carbon prepared by pyrolysis of sucrose in nitrogen at 1000°C, (b) carbon prepared by pyrolysis of anthracene at 1000°C. Insets show selected area diffraction patterns.[30]

P. J. F. Harris, *Crit. Rev. Solid State Mater. Sci.* 2005;30:235-253

Materiais carbonosos desordenados

Materiais grafitizáveis e não-grafitizáveis:

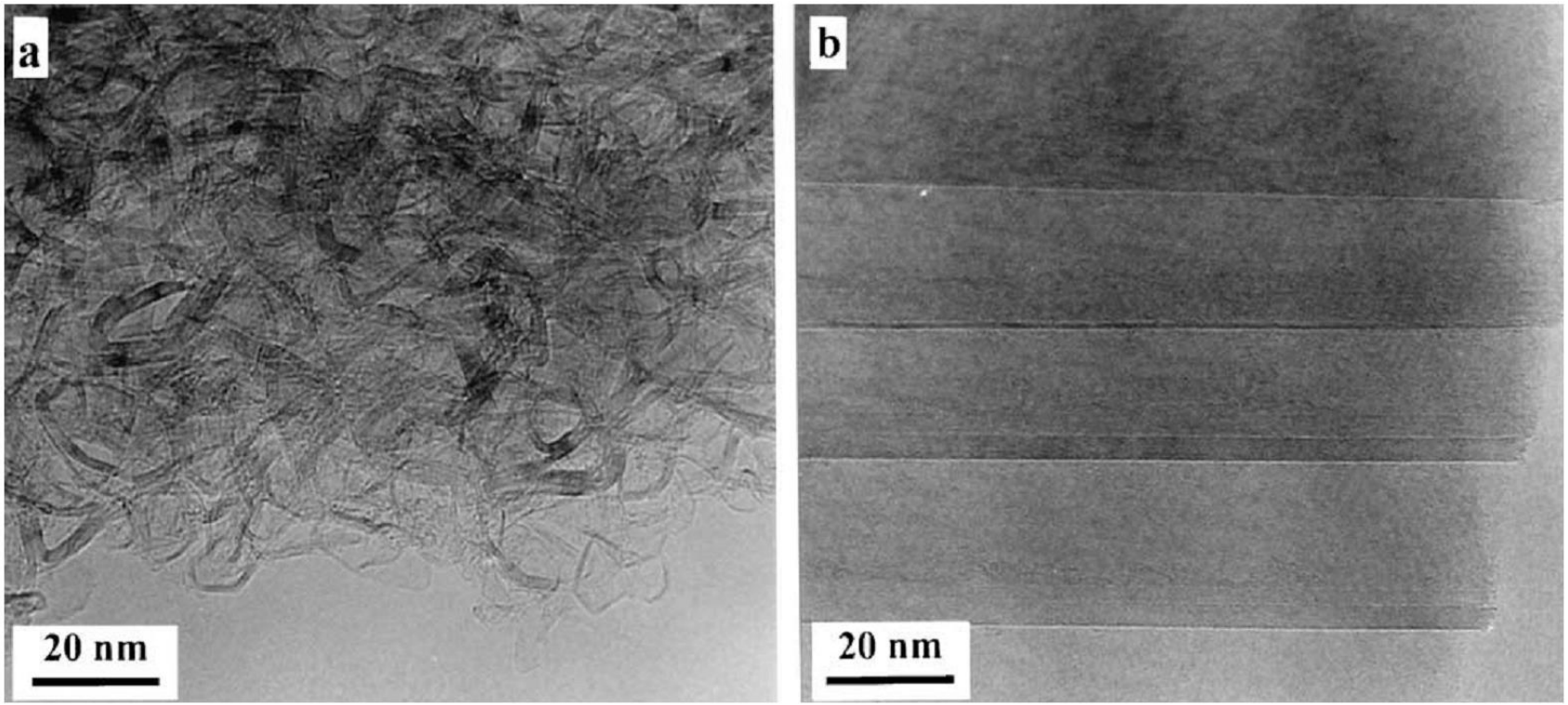


FIG. 8. Micrographs of (a) sucrose carbon and (b) anthracene carbon following heat treatment at 2300°C.

P. J. F. Harris, *Crit. Rev. Solid State Mater. Sci.* 2005;30:235-253

Materiais carbonosos desordenados

Modelos estruturais:

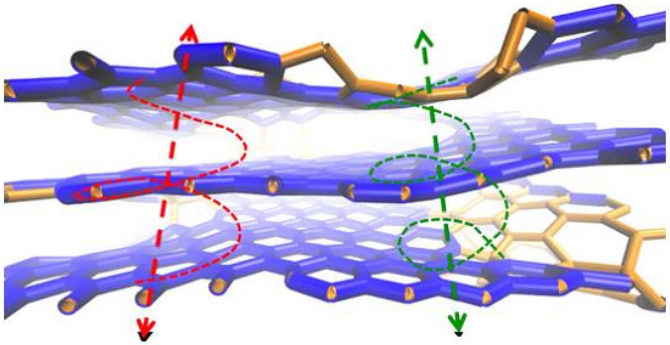


Fig. 7 – Chunk of the AP PyC model showing a screw dislocation pair (red and green dashed lines and arrows; chemical bonds are displayed with the same color code as in Figs. 3 and 4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

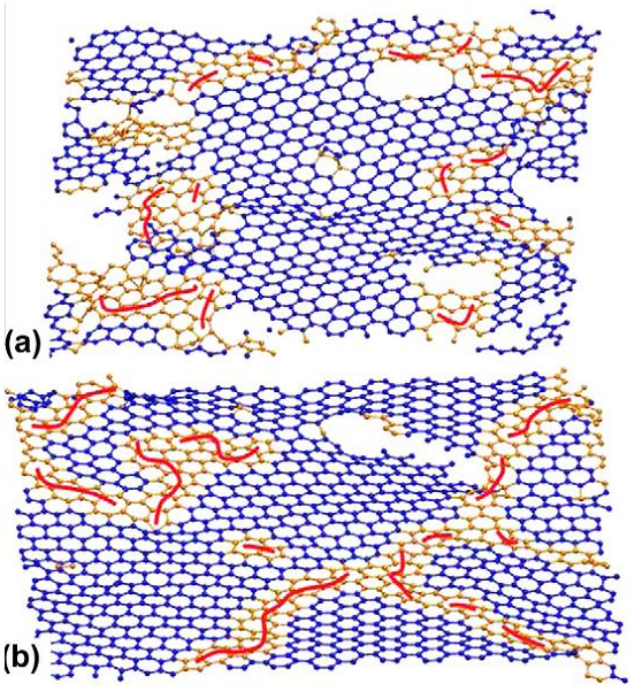


Fig. 8 – Carbon sheets (0.3 nm-thick in-plane slices) of the AP (a) and HT (b) PyC models (same color code as in Figs. 3 and 4; red lines indicate the pentagon/heptagon pairs and lines of pairs). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Leyssale et al., *Carbon* 2012;50:4388.

RMN em materiais de carbono

Alguns nuclídeos de interesse para estudos via RMN no estado sólido:

Nuclídeo	*Abundância natural* (%)	*Spin nuclear*	*Frequência de Larmor* [a] (MHz)	*Receptividade* [b]
^{1}H	99,99	1/2	100,000	1,000
^{7}Li	92,41	3/2	38,864	0,271
^{13}C	1,07	1/2	25,145	$1,70 \times 10^{-4}$
^{15}N	0,368	1/2	10,137	$3,84 \times 10^{-6}$
^{17}O	0,038	5/2	13,556	$1,11 \times 10^{-5}$
^{19}F	100	1/2	94,094	0,834
^{23}Na	100	3/2	26,452	$9,27 \times 10^{-2}$
^{29}Si	4,683	1/2	19,867	$3,68 \times 10^{-4}$
^{31}P	100	1/2	40,481	$6,65 \times 10^{-2}$
^{33}S	0,76	3/2	7,676	$1,72 \times 10^{-5}$
^{43}Ca	0,135	7/2	6,730	$8,68 \times 10^{-6}$
^{129}Xe	26,44	1/2	27,810	$5,72 \times 10^{-3}$

[a] Para um campo magnético estático de of 2,35 T (espectrômetro de RMN de 100 MHz).
[b] Relativa a ^{1}H.

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

RMN de ^{13}C no estado sólido

Deslocamentos químicos típicos em espectros de RMN de ^{13}C de materiais de carbono:

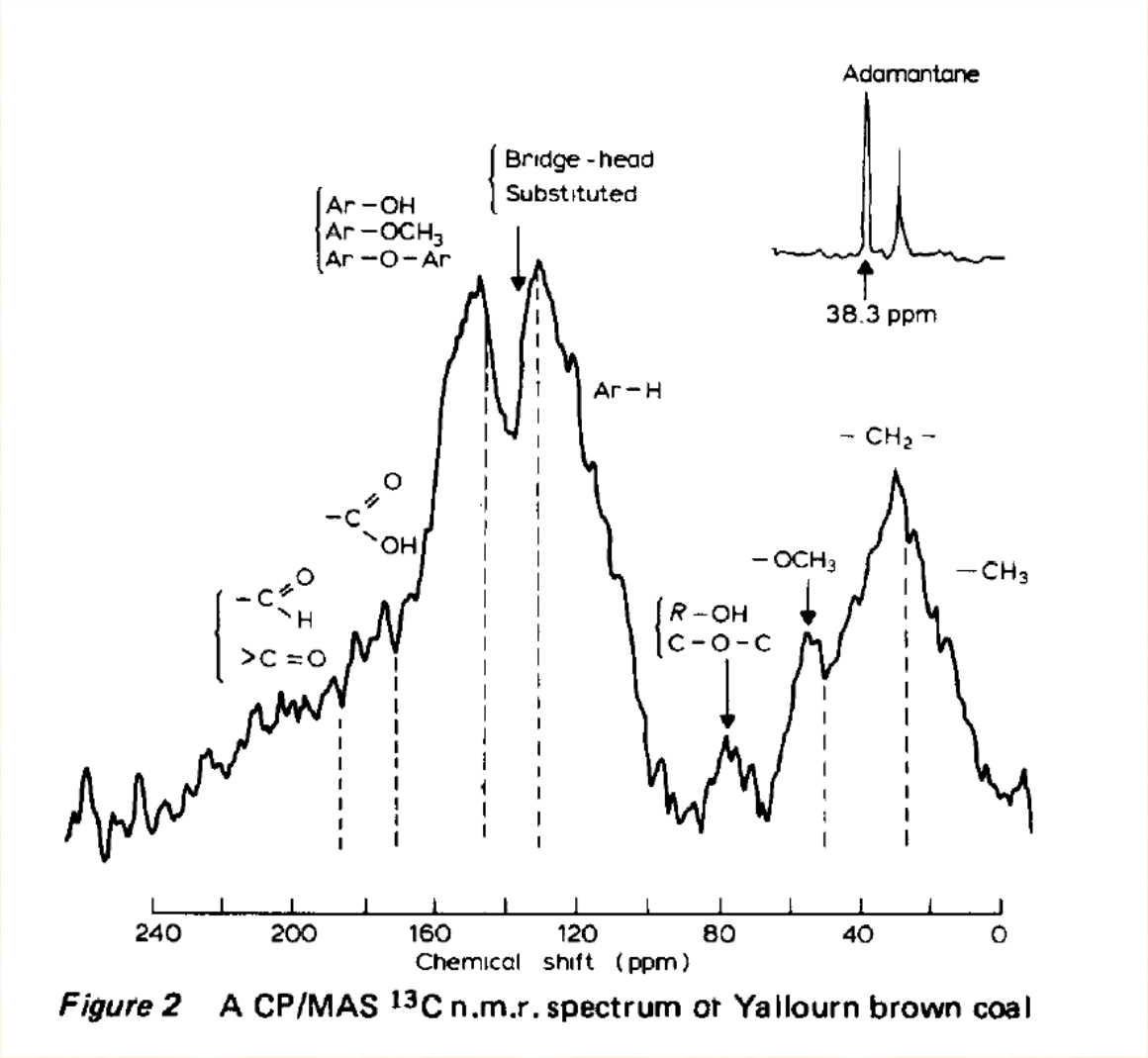


Figure 2 A CP/MAS ^{13}C n.m.r. spectrum of Yallourn brown coal

Yoshida et al., *Fuel* 1982;61:824

RMN de ^{13}C no estado sólido

Deslocamentos químicos típicos em espectros de RMN de ^{13}C de materiais de carbono:

TABLE 2.2

Isotropic Chemical Shifts (δ_C) for Some Chemical Groups Typically Found in Organic Matter and in Carbon Materials

Chemical Group	δ_C (ppm TMS)
$-CH_3$	0–23
$-CH_2-$	23–60
$-OCH_3$	50–60
–C–O–C–	70–95
$H-C_{aro}$	110–120
$C-C_{aro}^{*}$	130–140
$O-C_{aro}$	140–160
$C-(C^{*}=O)-OH$	160–180
$C-(C^{*}=O)-C,H$	180–220

Note: In the case of the presence of chemically distinct carbon atoms, the δ_C value corresponds to the atom indicated by an asterisk.

Freitas et al., *Chem. Phys. Carbon* 2012;31:85-169.

RMN de ^{13}C no estado sólido

Espectros obtidos para diferentes materiais de carbono:

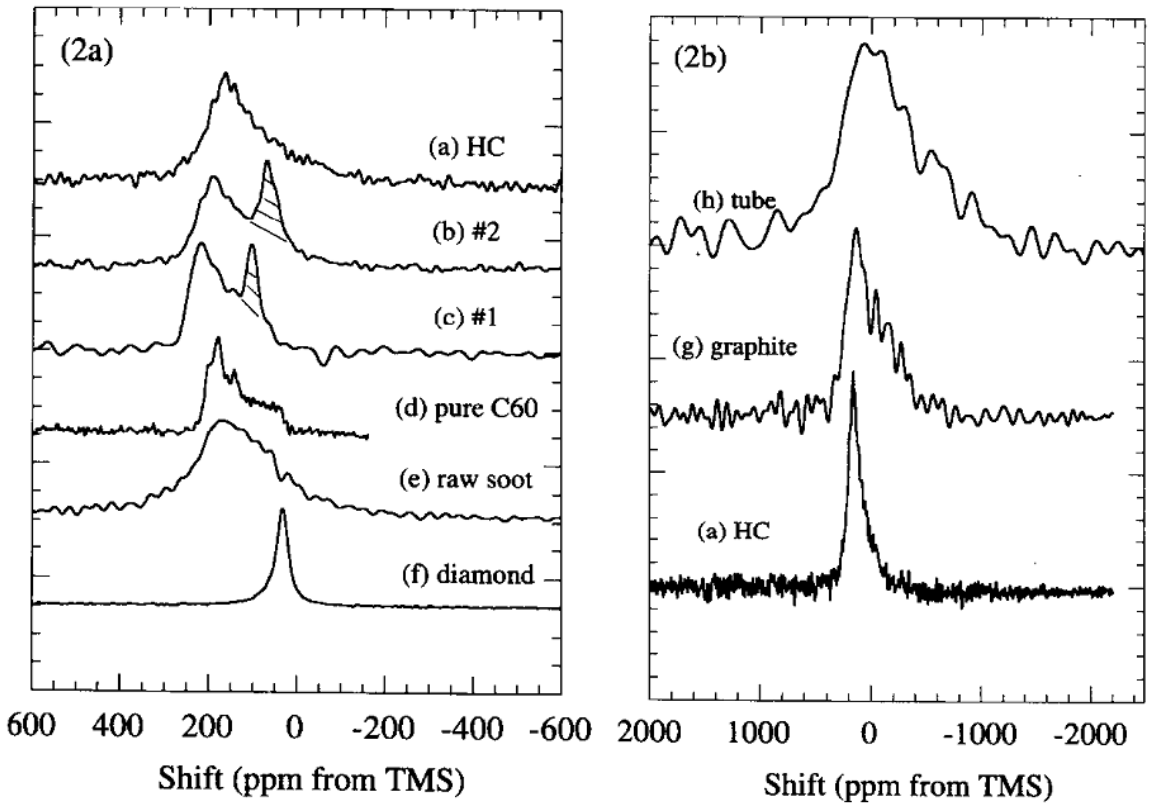
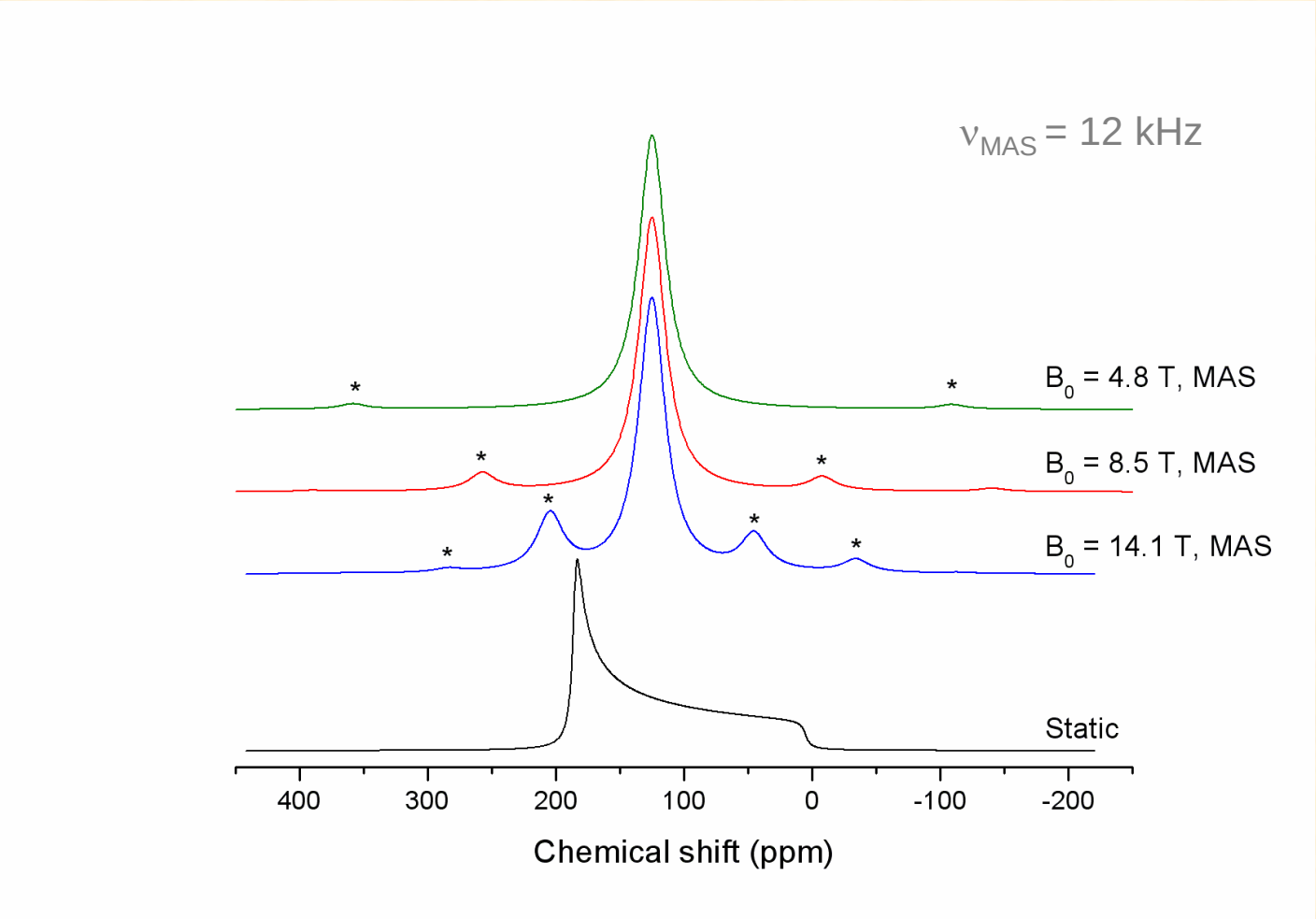


Fig. 2. ^{13}C-NMR spectra at low temperature. (a) Hard carbon at 4.2 K; (b) rhombohedral phase (No. 2) at 4.2 K; (c) FCC phase (No. 1) at 4.2 K; (d) pristine C_{60} at 77 K, (e) carbon raw soot obtained from MER Co. Ltd at 4.2 K; (f) diamond powder of 1 μm diameter at 130 K; (g) graphite powder at 4.2 K; and (h) randomly oriented bundle of carbon tube at 4.2 K.

Maniwa et al., *Carbon* 1996;34:1287-1291

RMN de ^{13}C no estado sólido

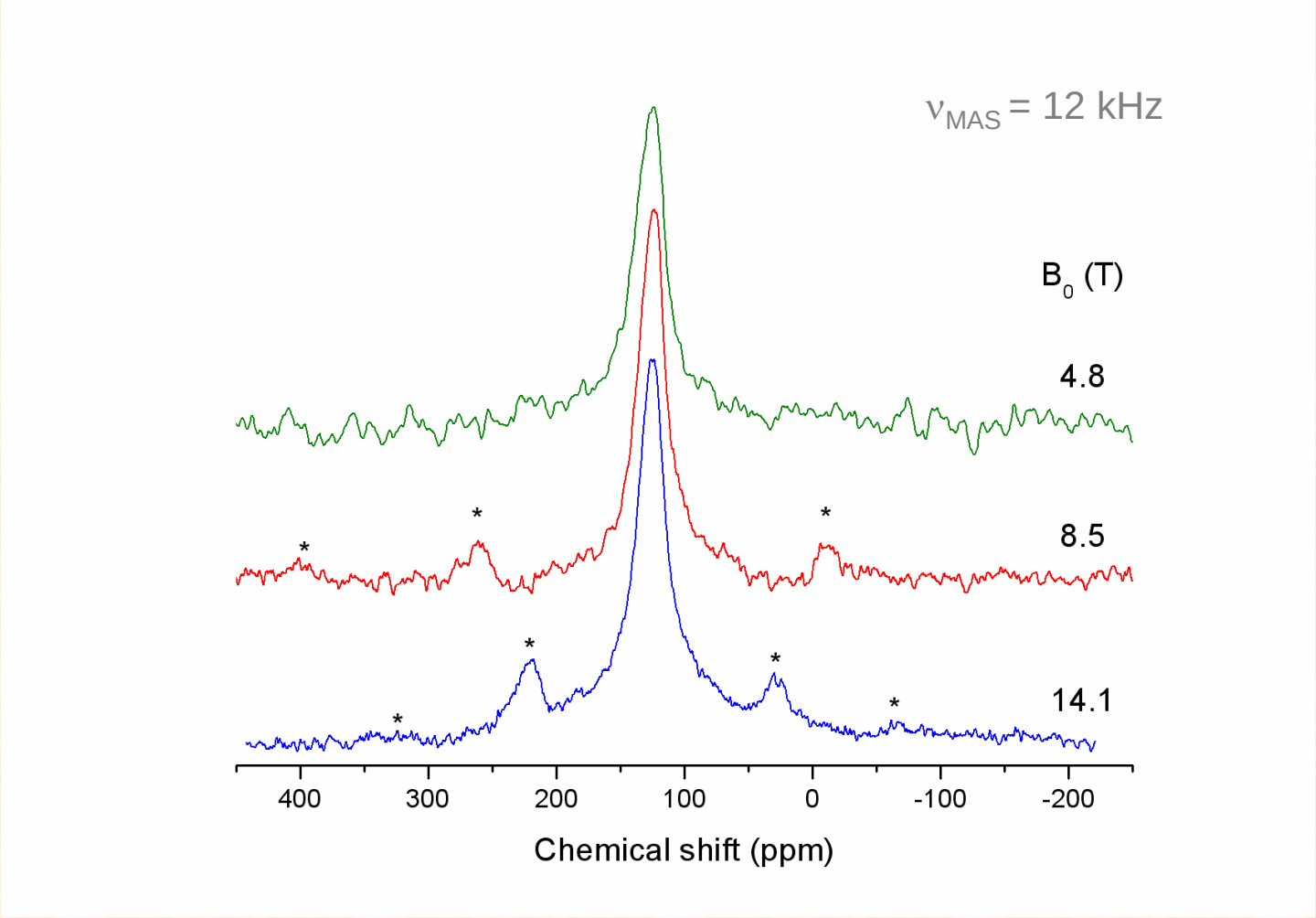
Espectros de RMN de ^{13}C simulados para uma plano grafeno – efeitos de CSA :



CSA: *Chemical Shielding Anisotropy*

RMN de ^{13}C no estado sólido

Espectros de RMN de ^{13}C – material carbonoso não-grafítico:



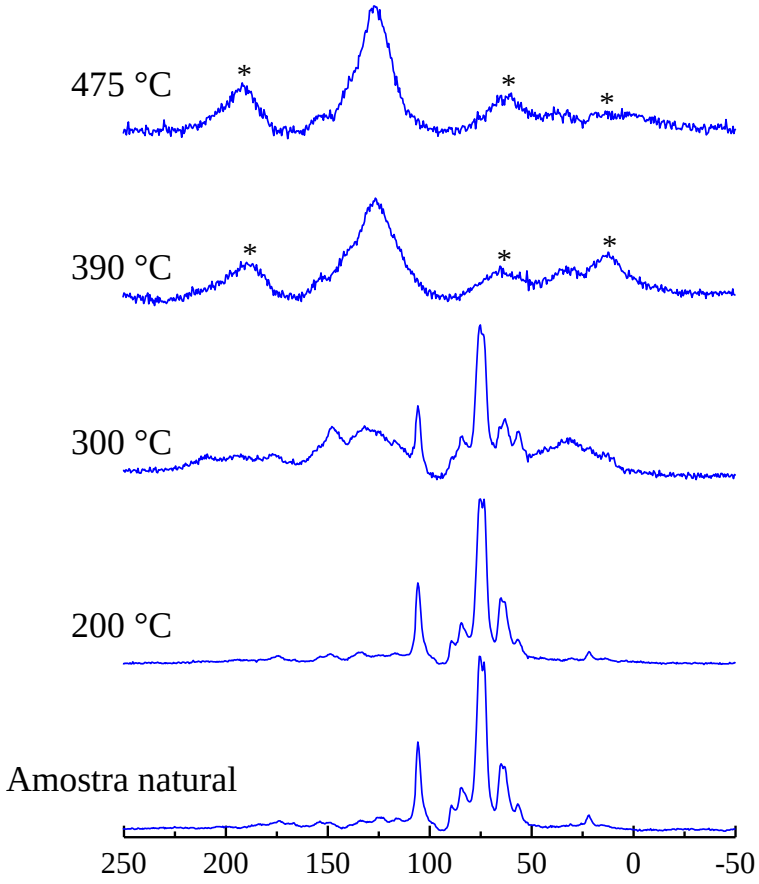
RMN de ^{13}C no estado sólido

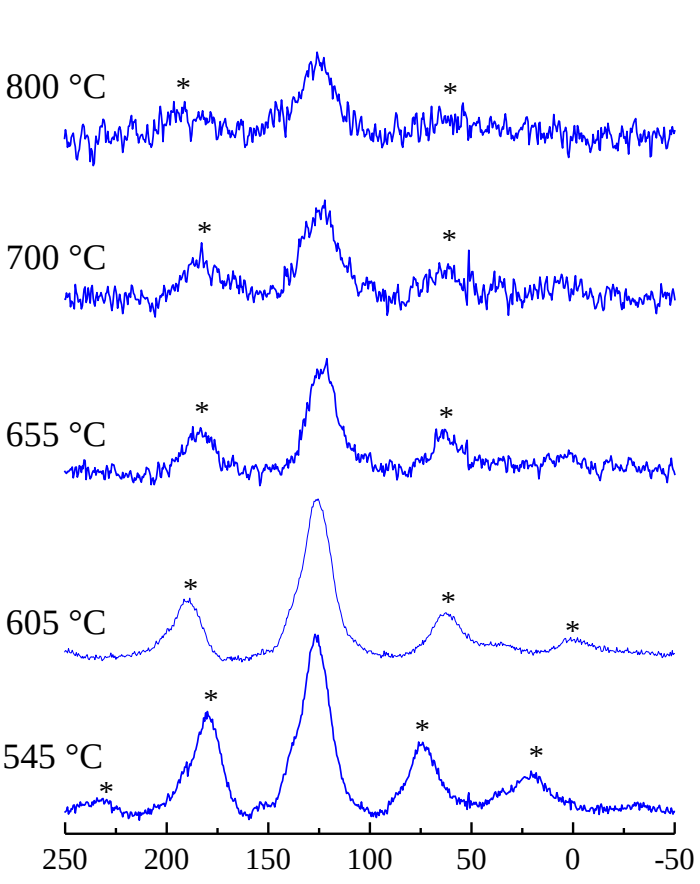
Efeitos de CSA para vários campos magnéticos estáticos:

B_0 (T)	$f_L(^1H)$ (MHz)	$f_L(^{13}C)$ (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

Processo de carbonização

Materiais derivados de casca de arroz – RMN de ^{13}C (CP/MAS):





Processo de carbonização

Materiais obtidos por tratamentos térmicos – RMN de ^{13}C:

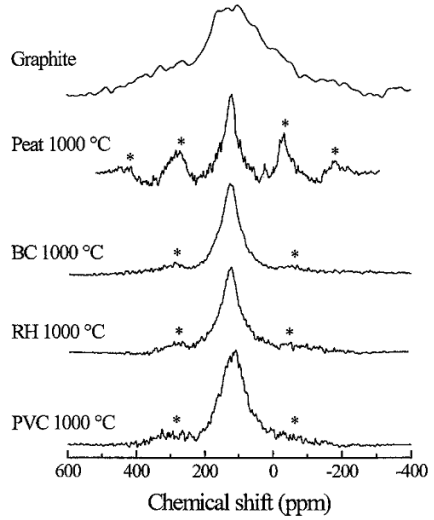


FIG. 1. ^{13}C MAS NMR spectra of polycrystalline graphite and heat-treated carbon samples (prepared from the various precursors at the indicated HTTs). Asterisks denote spinning sidebands.

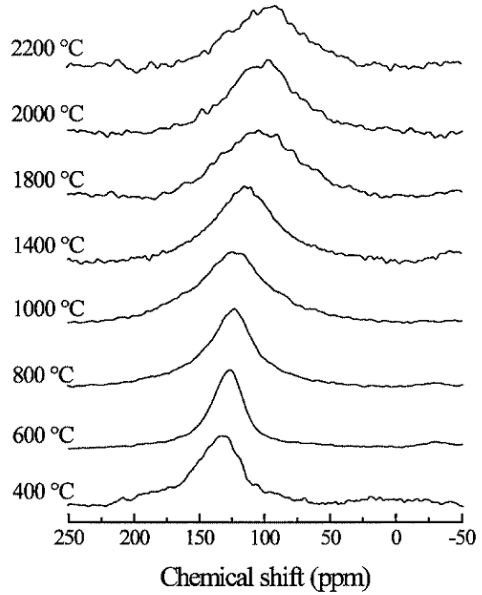
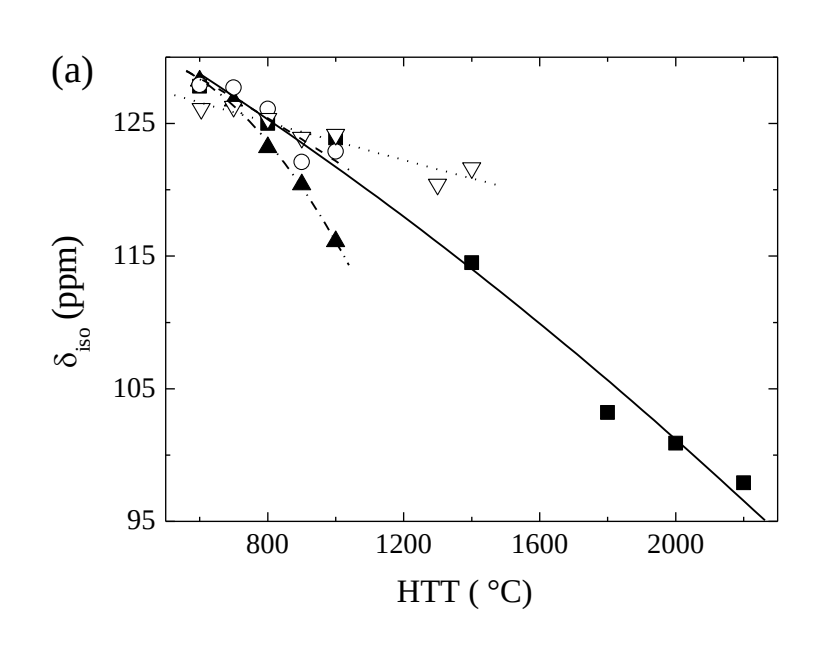


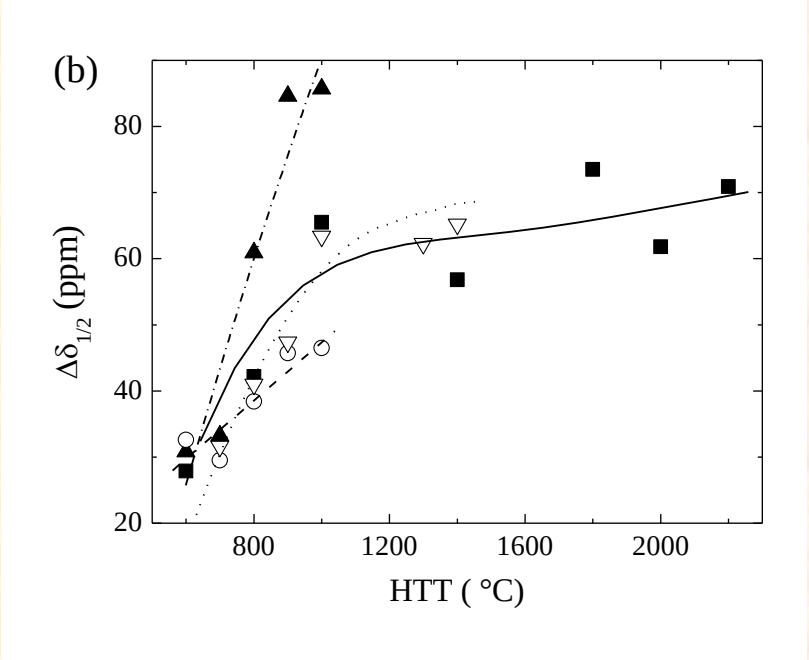
FIG. 2. ^{13}C MAS NMR spectra of BC samples prepared at the indicated HTTs.

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

Processo de carbonização

Materiais obtidos por tratamentos térmicos – RMN de ^{13}C:





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Processo de carbonização

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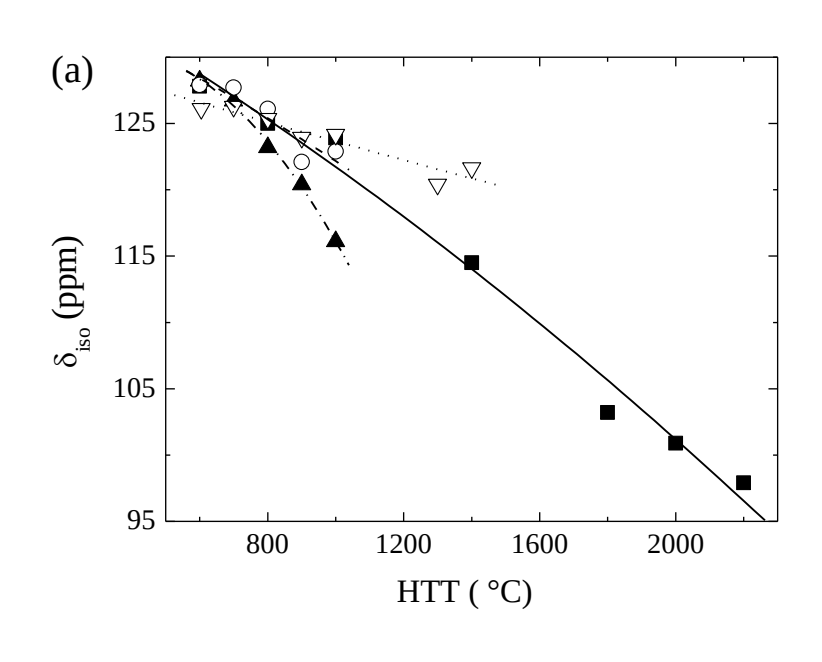

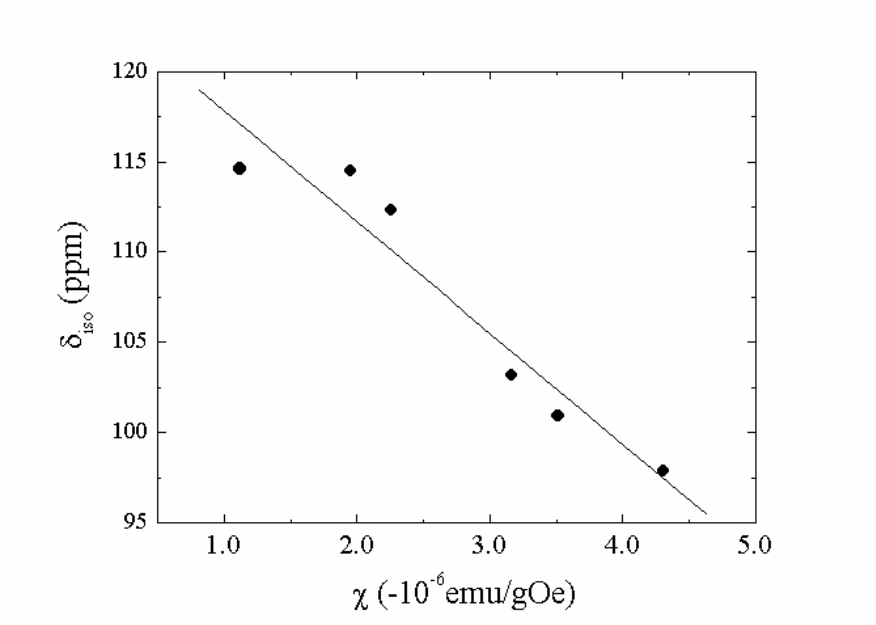

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Carvões ativados

- Sólidos estruturalmente desordenados com rede de poros irregular.
- Distribuiçoes de macroporos, mesoporos e microporos.
- Applicações: suporte de catalisadores, tratamento de água, armazenamento de gases, ...
- Composição básica: C, H, O (majoritários), N, S, ...
- Matéria mineral (cinzas): depende do precursor e da preparação.

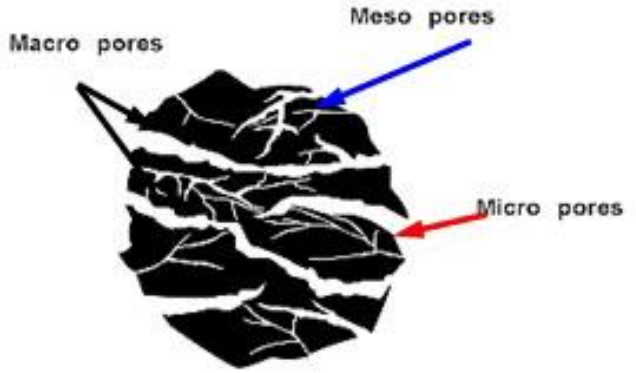

Figure 1: Activated carbon structure - schematic.

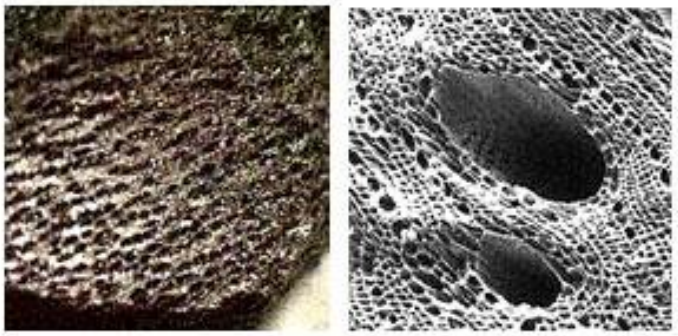

Figure 2: Activated carbon structure – SEM pictures.

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

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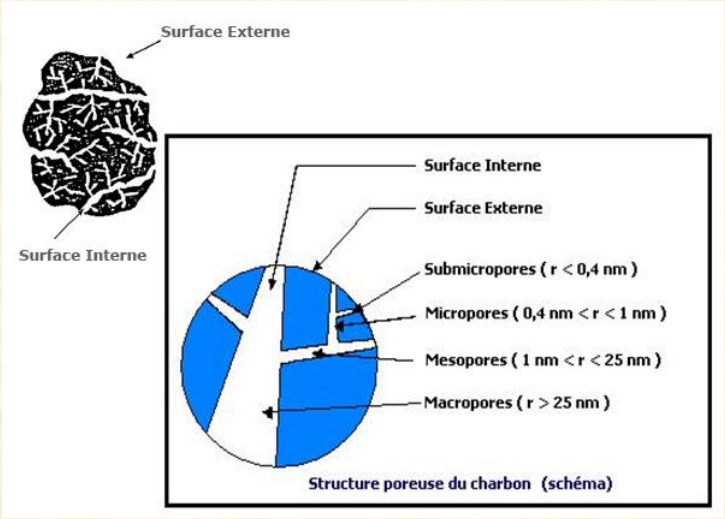
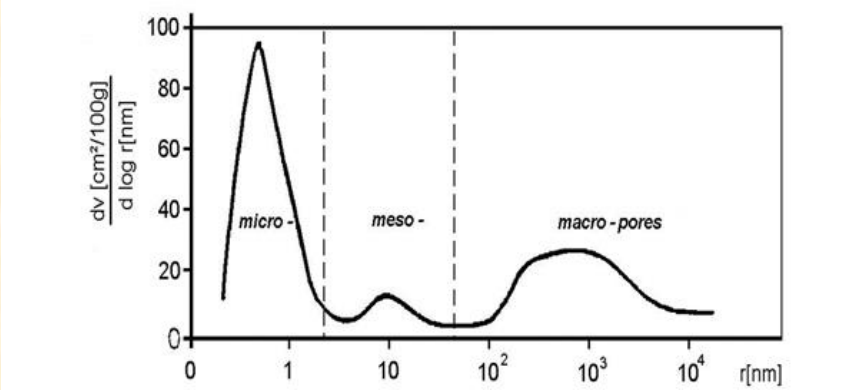




http://www.asseau.com/en/03-9.html

Carvões ativados

– Preparação:

- Ativação física: vapor d'água, ar, CO_2,…
- Ativação química: H_3PO_4, NaOH, KOH, $CaCl_2$, …
- Precursores: carvões minerais, mineral, antracito, carvões vegetais, materiais lignocelúlósicos, …
- Etapas típicas: impregnação, tratamentos térmicos, lixiviação, secagem, tratamentos químicos posteriores, …
- Presença de elementos "inorgânicos": Na, K, Ca, P, …
  - ✓ Relacionada à matétia mineral no precursor e aos reagents utilizados na ativação química.
  - ✓ Influencia as características químicas superficiais do carvão ativado.

Preparação de carvões ativados

Precursor de origem vegetal — Casca de arroz, palha de café, endocarpo de babaçu, ...

↓

Carbonização — 400-500°C, 1-4h, fluxo de N_2.

↓

Impregnação em meio aquoso — H_3PO_4, NaOH, ...

↓

Tratamento térmico de ativação — 400-900°C, 0,5-2h, fluxo de N_2.

↓

Lixiviação — Água destilada, soluções ácidas, ...

Material carbonoso poroso

Caracterização:

- Análise elementar.
- Análises térmicas.
- Adsorção de N_2 a 77K.
- MEV, DRX.
- RMN no estado sólido:
  ^{13}C, ^{23}Na, ^{29}Si, ^{31}P, ...

Grupos superficiais em carvões ativados

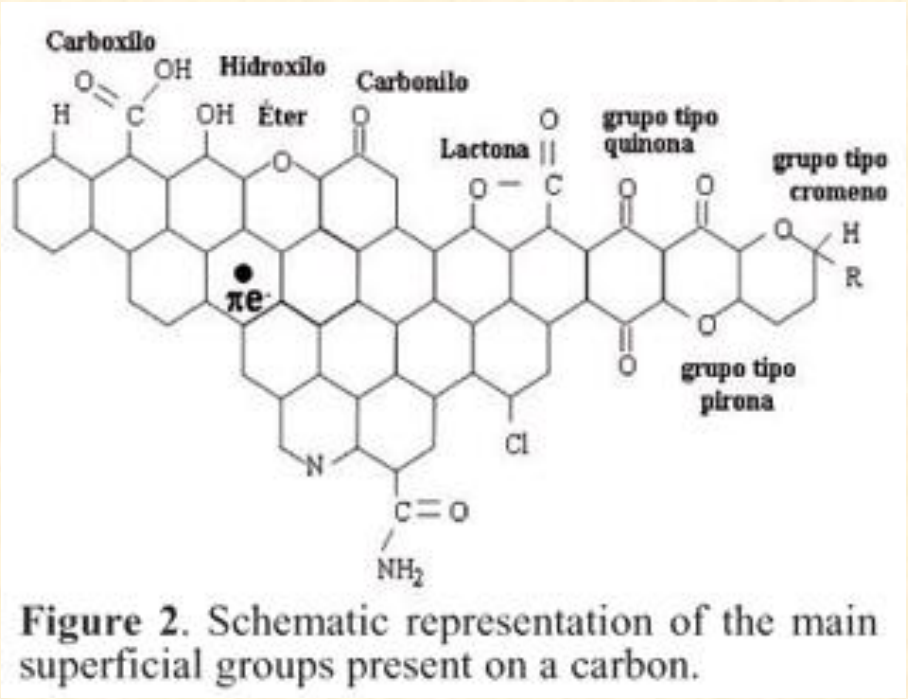
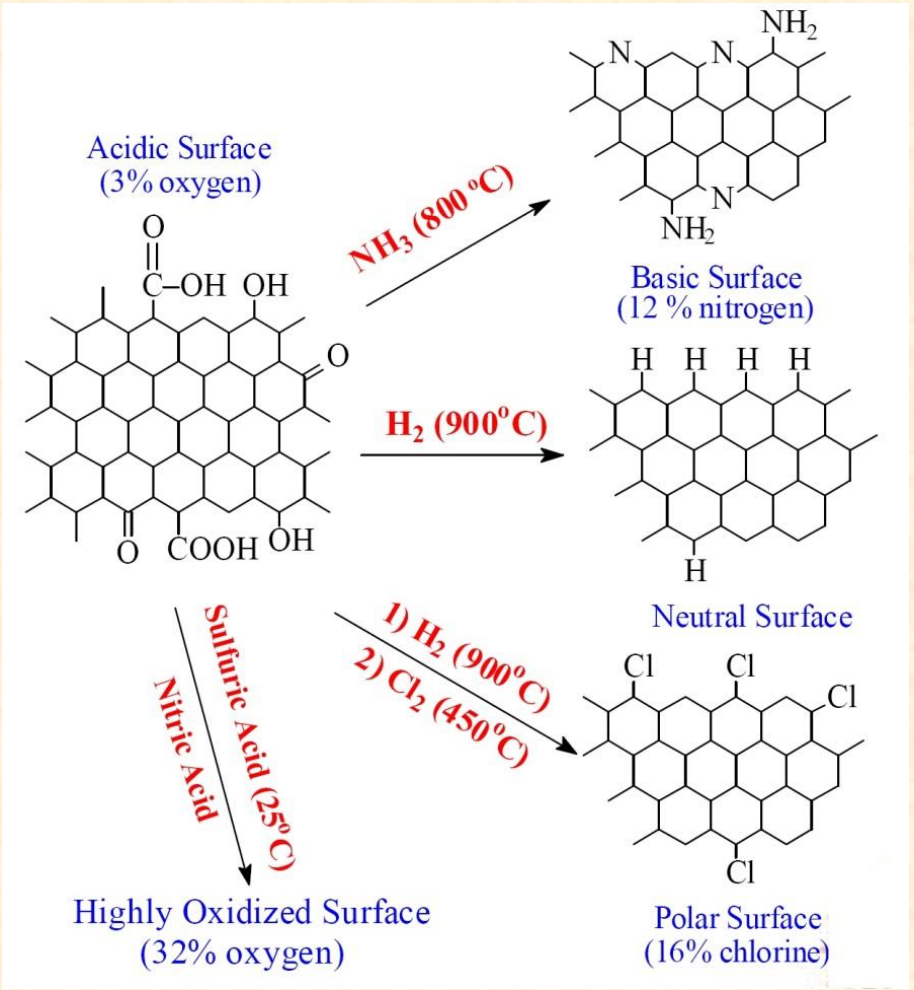


Figure 2. Schematic representation of the main superficial groups present on a carbon.

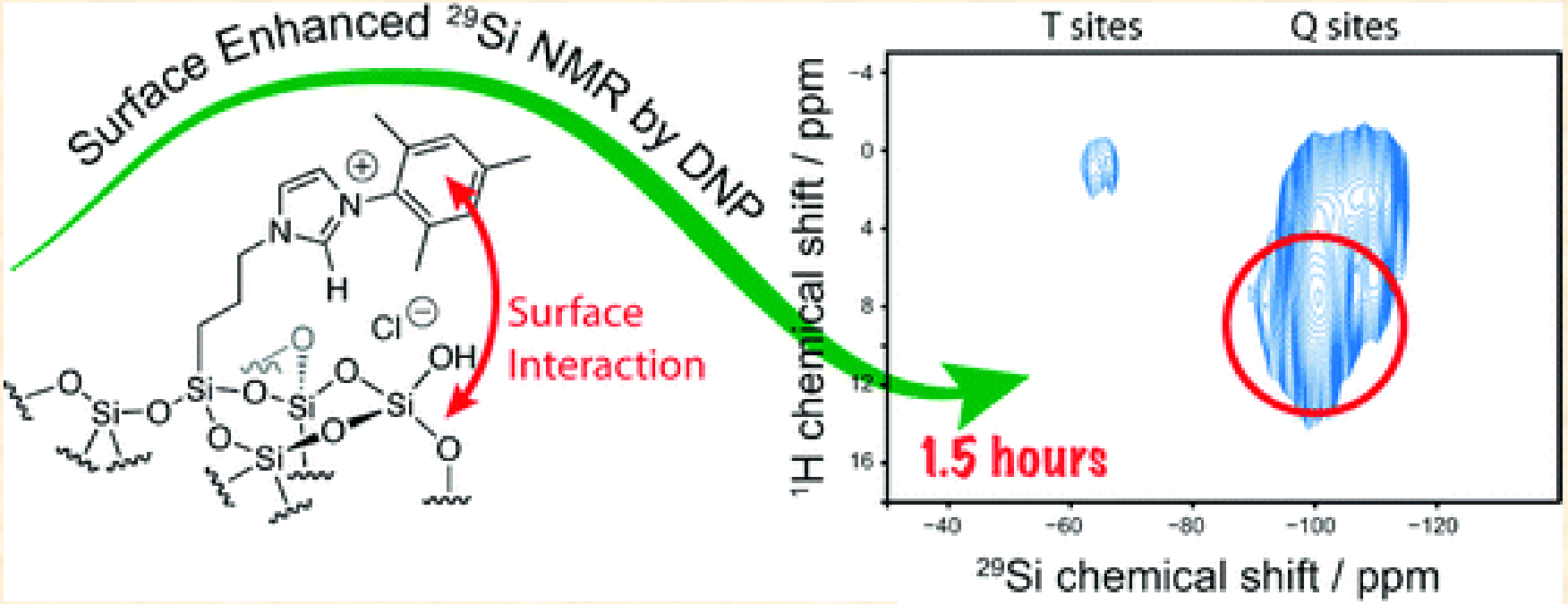
Cárdena-López et al., *Ecl. Quim. 2007;*32:61



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

Grupos superficiais em carvões ativados

Uso de RMN com polarização dinâmica nuclear (DNP): ***SENSNMR***



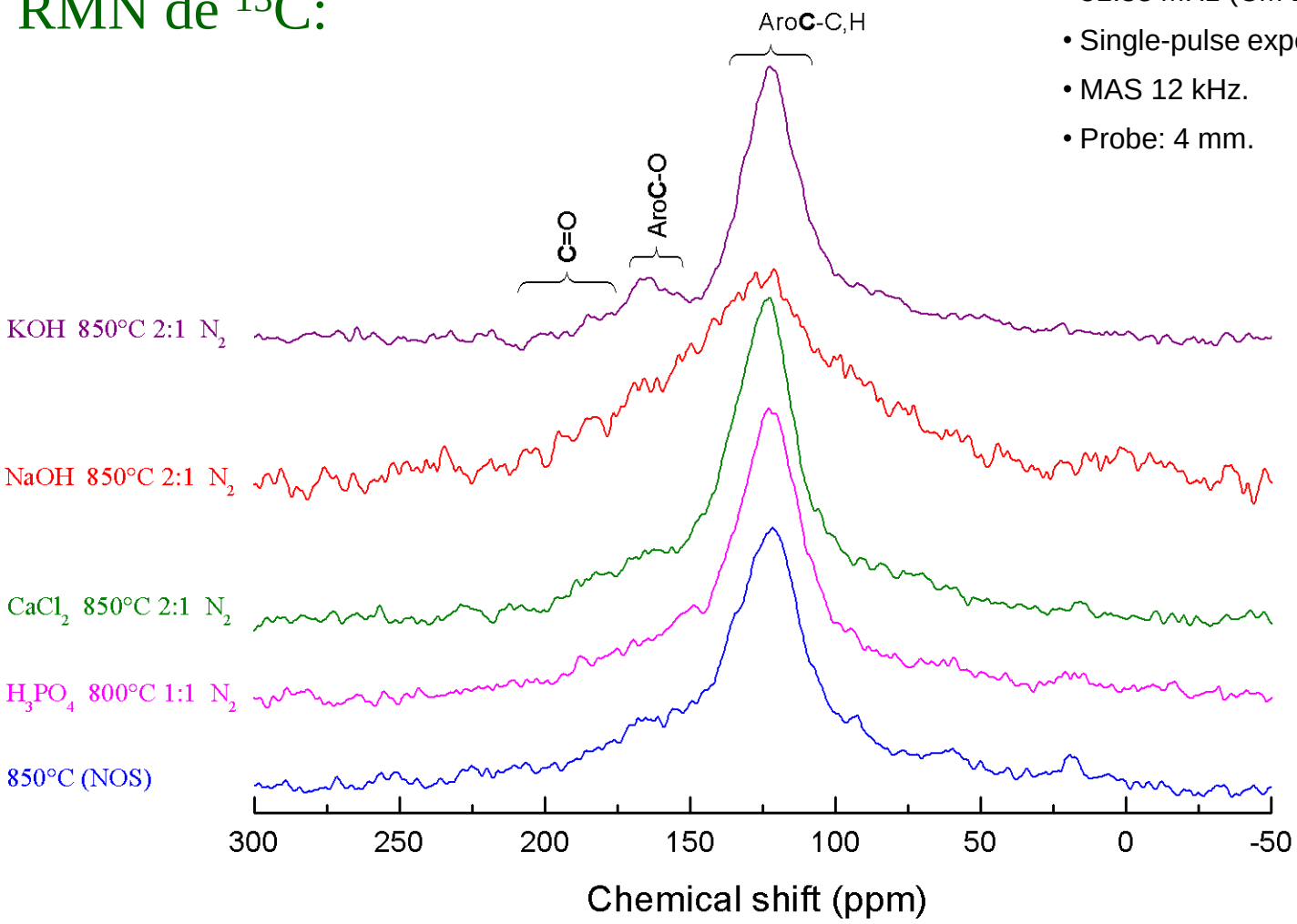
Emsley et al., *J. Am. Chem. Soc.* 2011;133:2104

- ✓ Impregnação incipiente do material poroso (sílica, alumina, etc.) com uma solução contendo o agente polarizador (com radicais livres).
- ✓ Técnica promissora para materiais de carbono porosos?

Carvões ativados

RMN de ^{13}C:

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



Carvões ativados

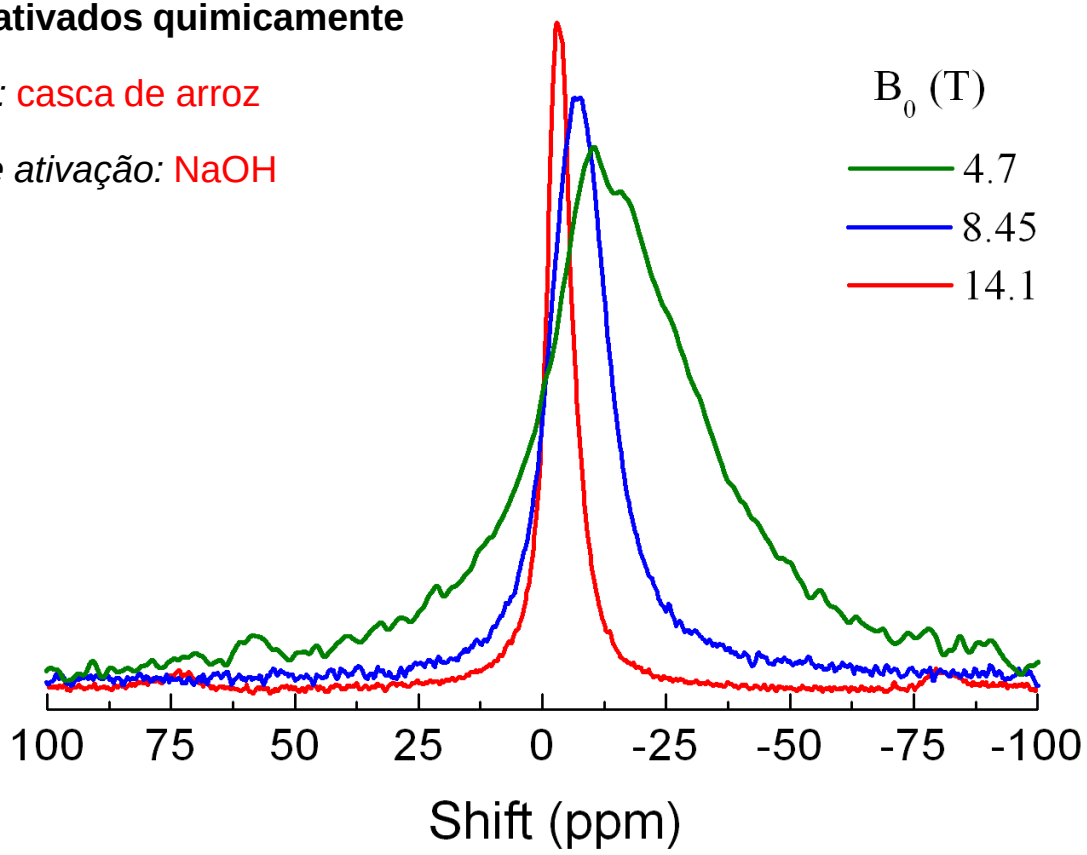
RMN de ^{23}Na:

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

Carvões ativados quimicamente

Precursor: casca de arroz

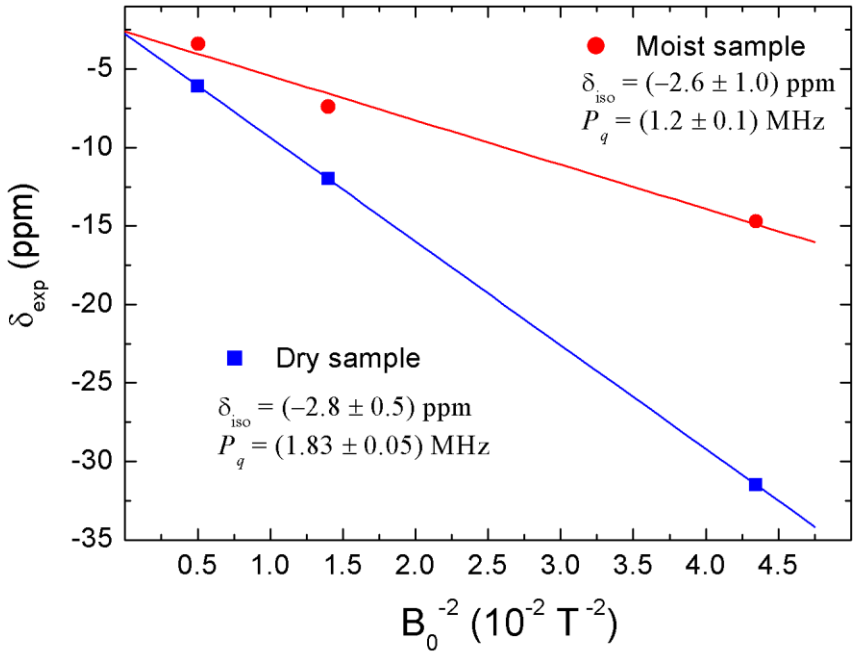
Agente de ativação: NaOH



Materiais estruturalmente desordenados: espectros sem singularidades características da interação quadrupolar.

Carvões ativados

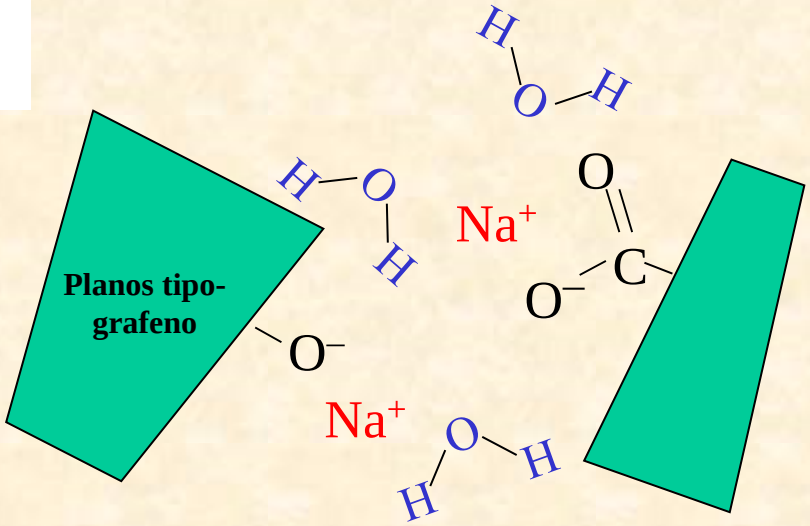
RMN de ^{23}Na:



- ✓ Deslocamentos químicos isotrópicos característicos de íons Na^+ ligados a grupos oxigenados.
- ✓ Possível existência de grupos superficiais contendo ligações do tipo Na-O-C nas bordas dos planos tipo-grafeno.
- ✓ Forte influência do grau de hidratação no gradiente de campo elétrico nos núcleos ^{23}Na.

$$\delta_{exp} = \delta_{iso} - 25000 \frac{C_q^2(1+\eta_q^2/3)}{(\gamma/2\pi)^2} \frac{1}{B_0^2}$$

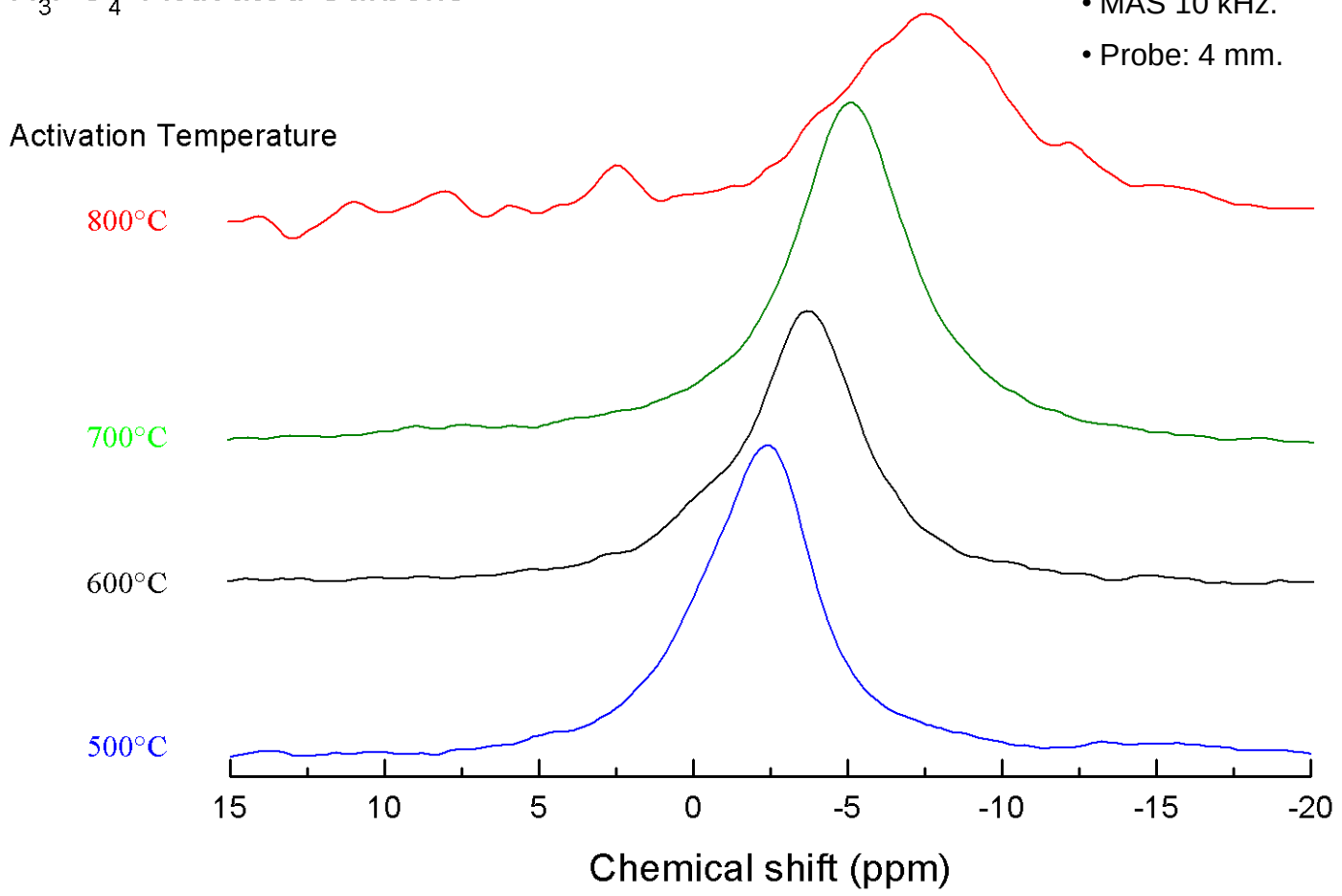
Freitas et al., *SSNMR* 2007;32:109



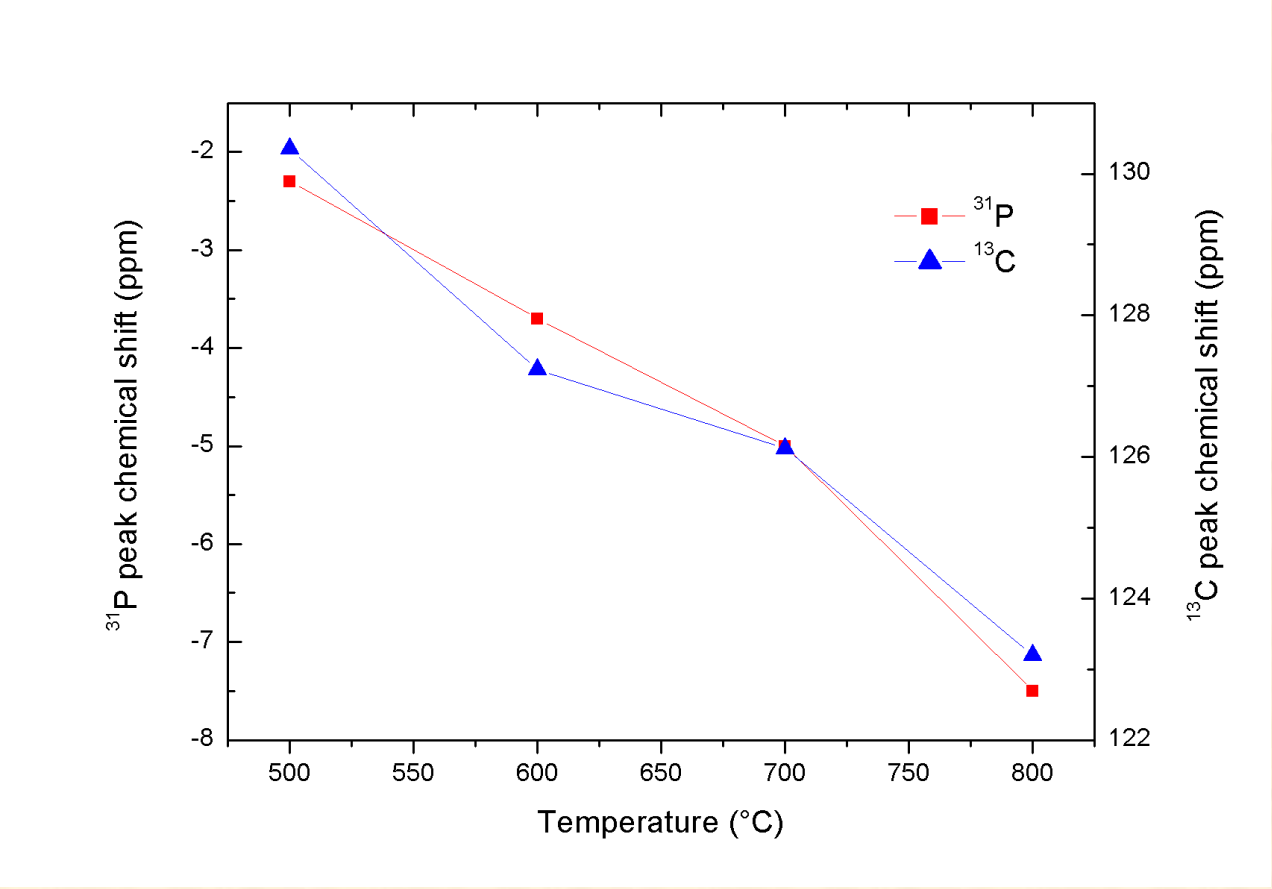
Carvões ativados

RMN de ^{31}P:

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



Efeito da temperatura de ativação



Comportamento ditado pelo crescimento da suscetibilidade diamagnética localmente anisotrópica dos planos tipo-grafeno.

Espécies adsorvidas em carvões ativados

RMN de ^{1}H:

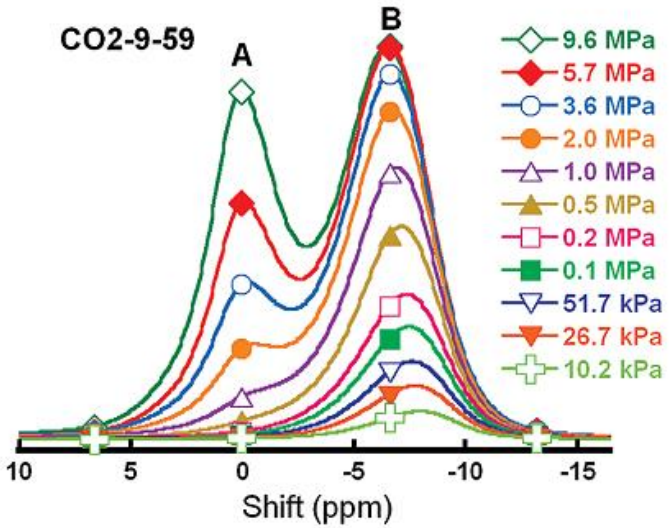


Figure 1. Evolution of the NMR spectra as a function of pressure for CO2-9-59 at 100 K. Peak A on the left evolves linearly with pressure and does not have a significant contribution at low pressures, while peak B is present even at the lowest pressure and approaches saturation at higher pressures.

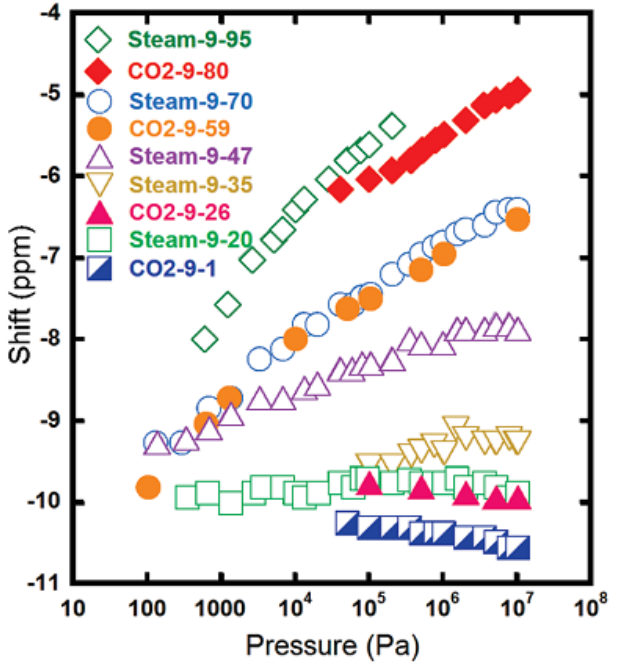


Figure 3. Chemical shift of the micropore peak versus pressure at 100 K. A noticeable change in shift with varied pressure is expected only in samples whose average pore size is larger than ~1.2 nm. All nine samples appear to have the same low-pressure limit of about −10 ppm, indicating little variation in the degree of graphitization of the adsorbent surface. The error of the shift is approximately ±0.2 ppm and is represented by the size of the data points.

Anderson et al., *J. Amer. Chem. Soc.* 2010;132:8618-8626

Espécies adsorvidas em carvões ativados

RMN de ^{1}H:

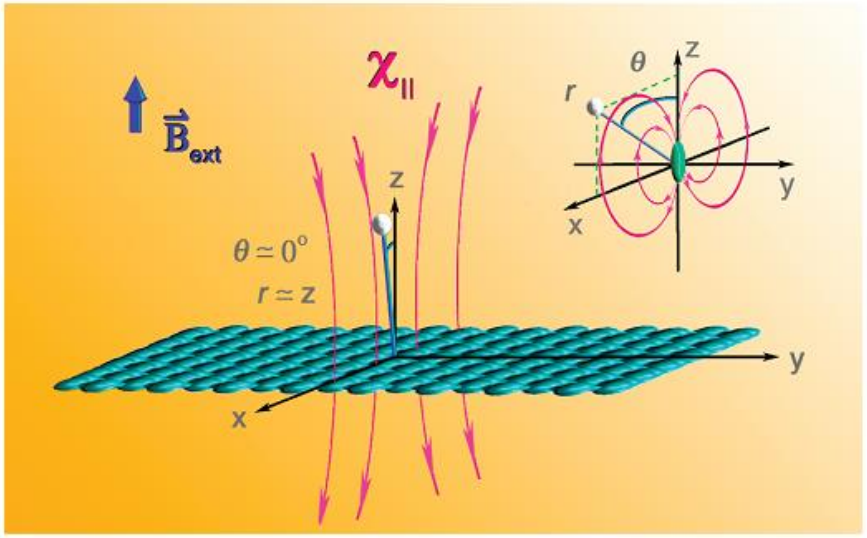
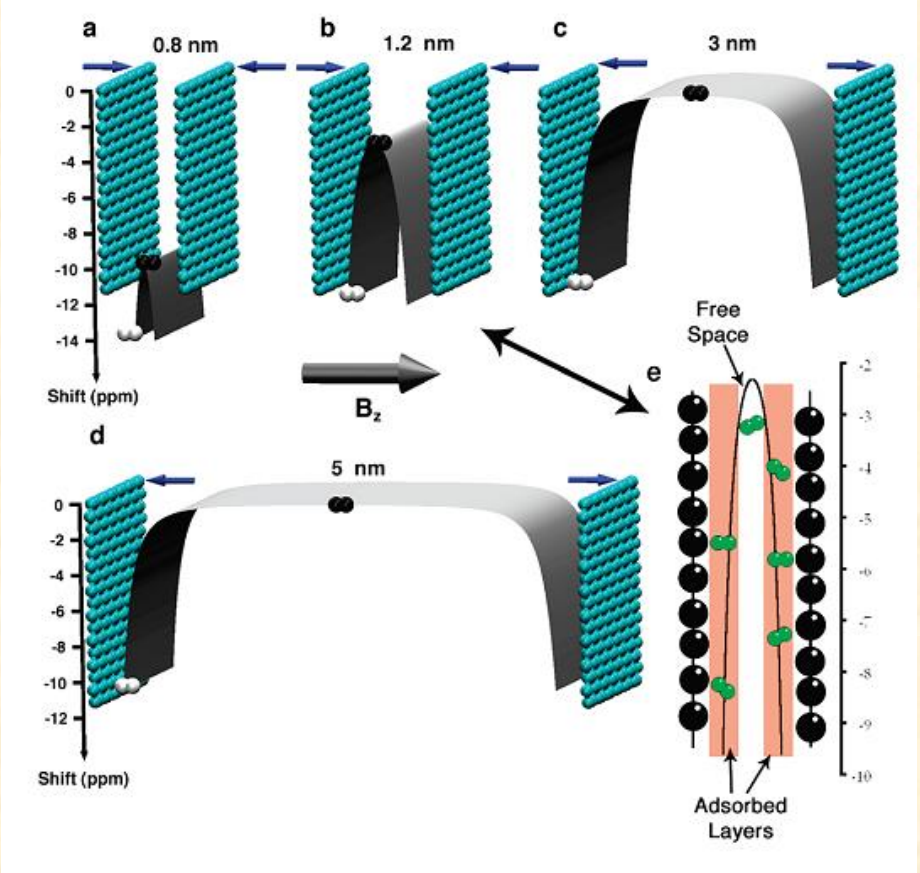


Figure 4. Upper right: Normally, a molecular grouping with an axially symmetric susceptibility tensor has tensor components which are dependent on r, the radial distance of the probe molecule from the center of the grouping; θ, which is the angle between the z-axis and the location of the probe molecule in the $x-z$ plane; and $\chi_{\perp}$ and $\chi_{\parallel}$, which are the molar magnetic susceptibilities of the grouping perpendicular and parallel to the z-axis, respectively ($\chi_{\parallel}$ shown here). Center: For a H_2 molecule adsorbed above a graphene plane and experiencing a local field due to the locally induced dipoles in the plane, $\theta \approx 0°$ and $r \approx z$, corresponding to the vertical distance from the plane.



Anderson et al., *J. Amer. Chem. Soc.* 2010;132:8618-8626

Biocarvões

Terra Preta de Índio

Solo da Região Amazônica

Figura 3. Contraste entre as terra pretas de índios e solos adjacentes da Região Amazônica[7]

Mandrich et al., *Rev. Virtual Quim.* 2011;3:426-433

Biocarvões

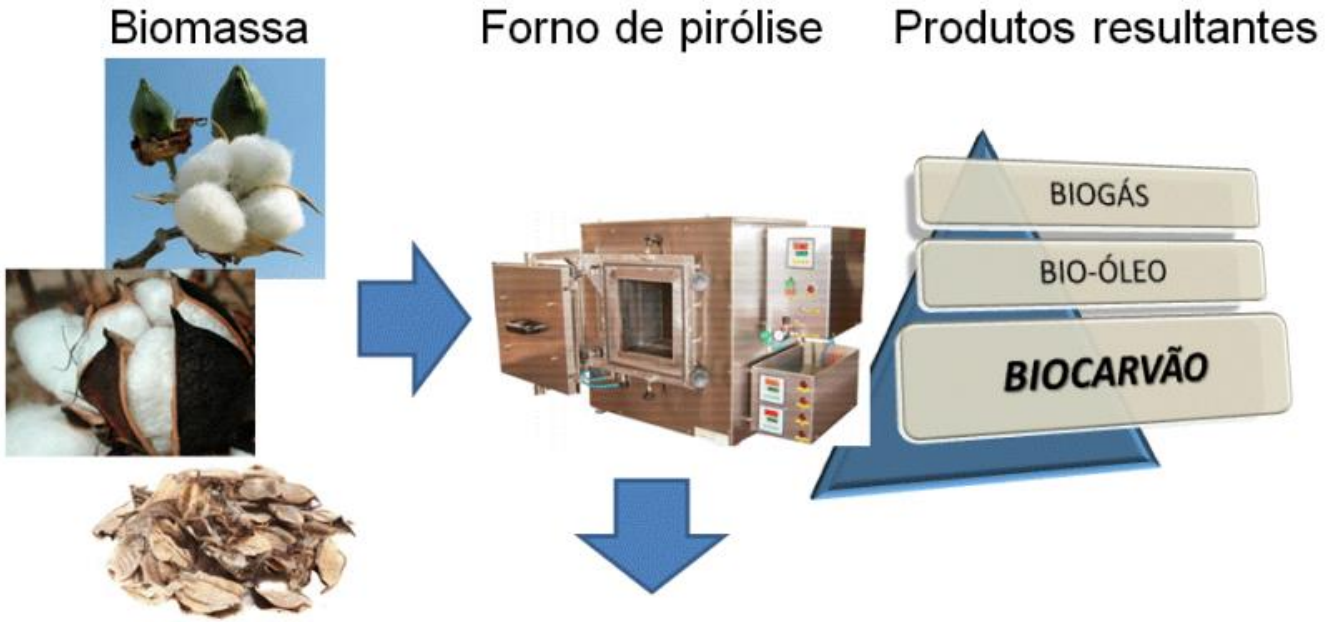


Figura 5. Esquema representativo para o estudo de produção de biocarvão, bio-óleo e biogás em laboratório, a partir de diferentes tipos de biomassas.[19]

Mandrich et al., *Rev. Virtual Quim.* 2011;3:426-433

Biocarvões

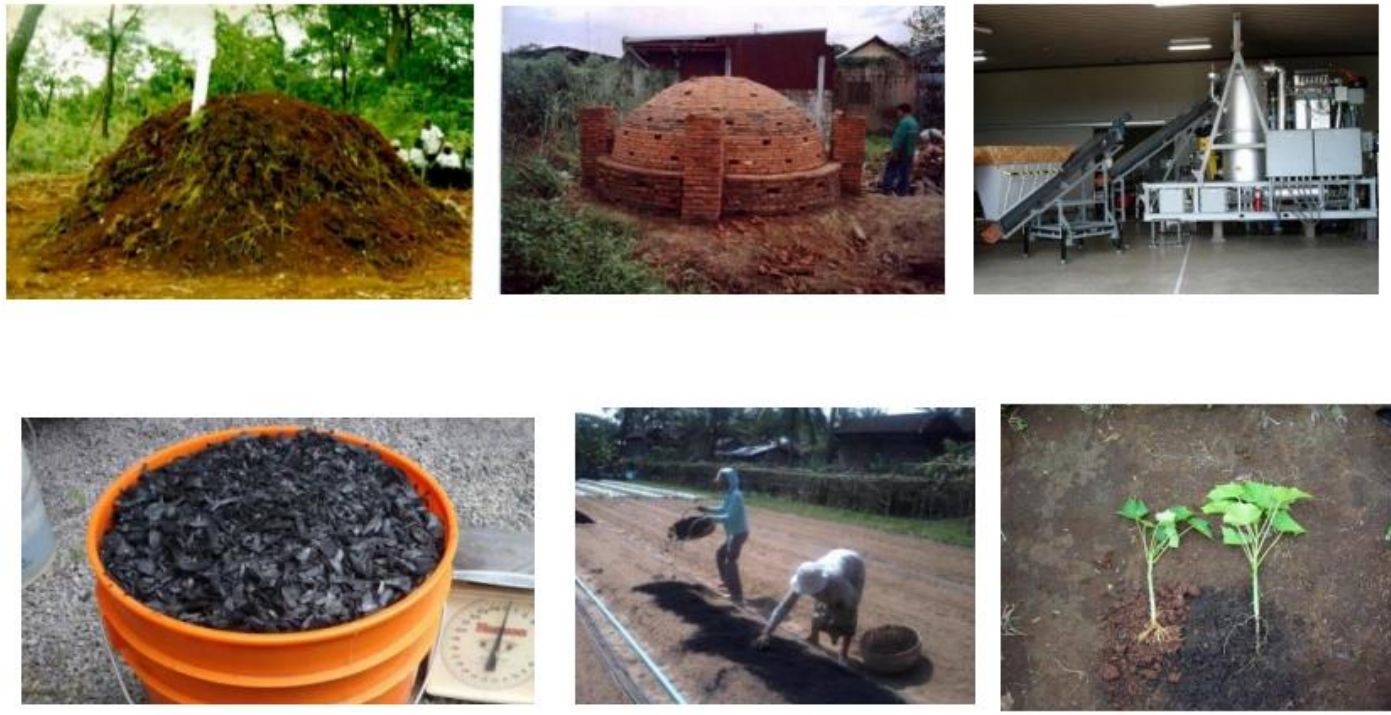
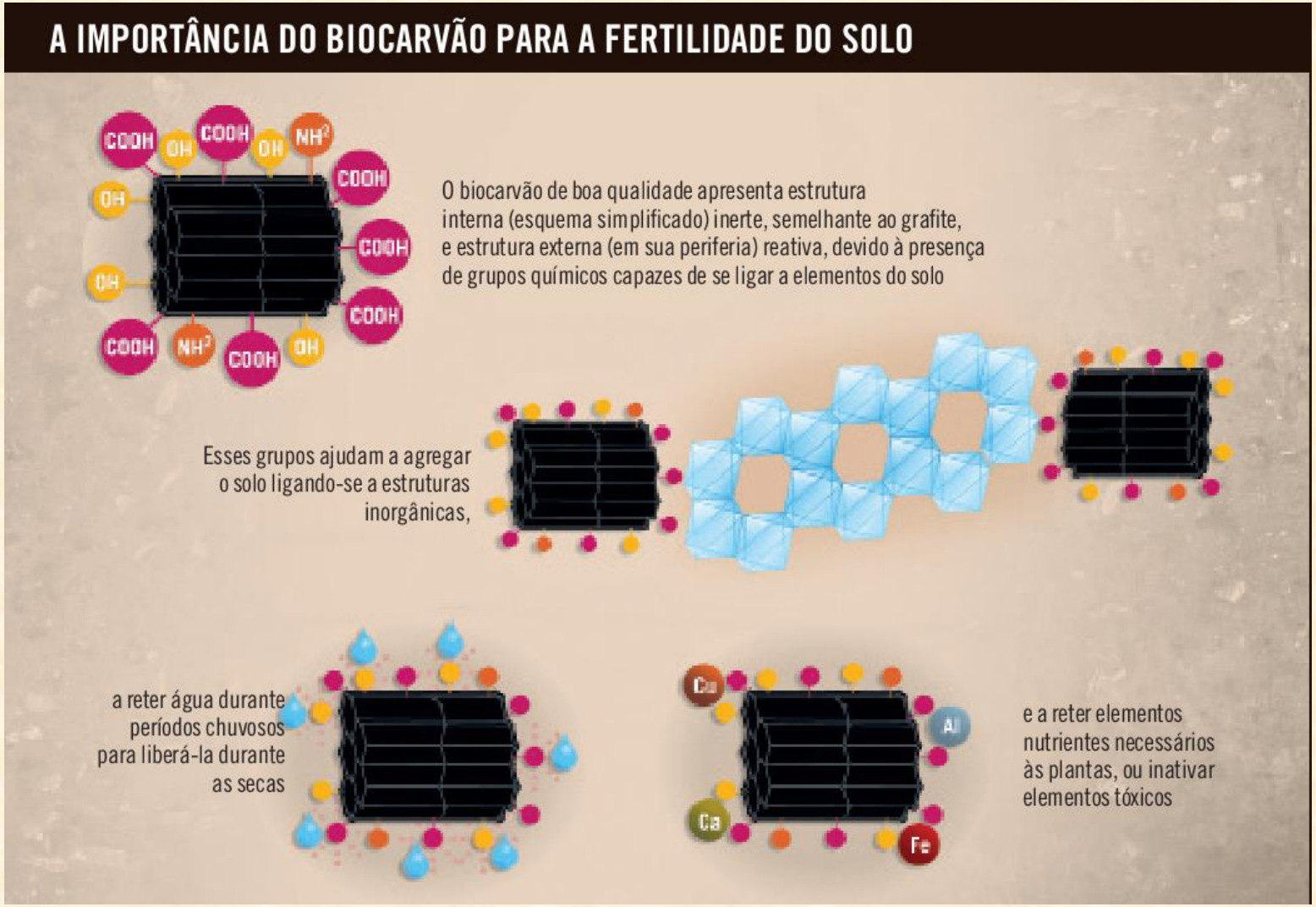


Figura 6. Produção industrial de biocarvão por pirólise (ausência de oxigênio) da biomassa (acima) e uso do biocarvão (abaixo).[20]

Mandrich et al., *Rev. Virtual Quim.* 2011;3:426-433

Biocarvões



Mandrich, *Ciência Hoje* 2011;47:48-52

Biocarvões

RMN de ^{13}C:

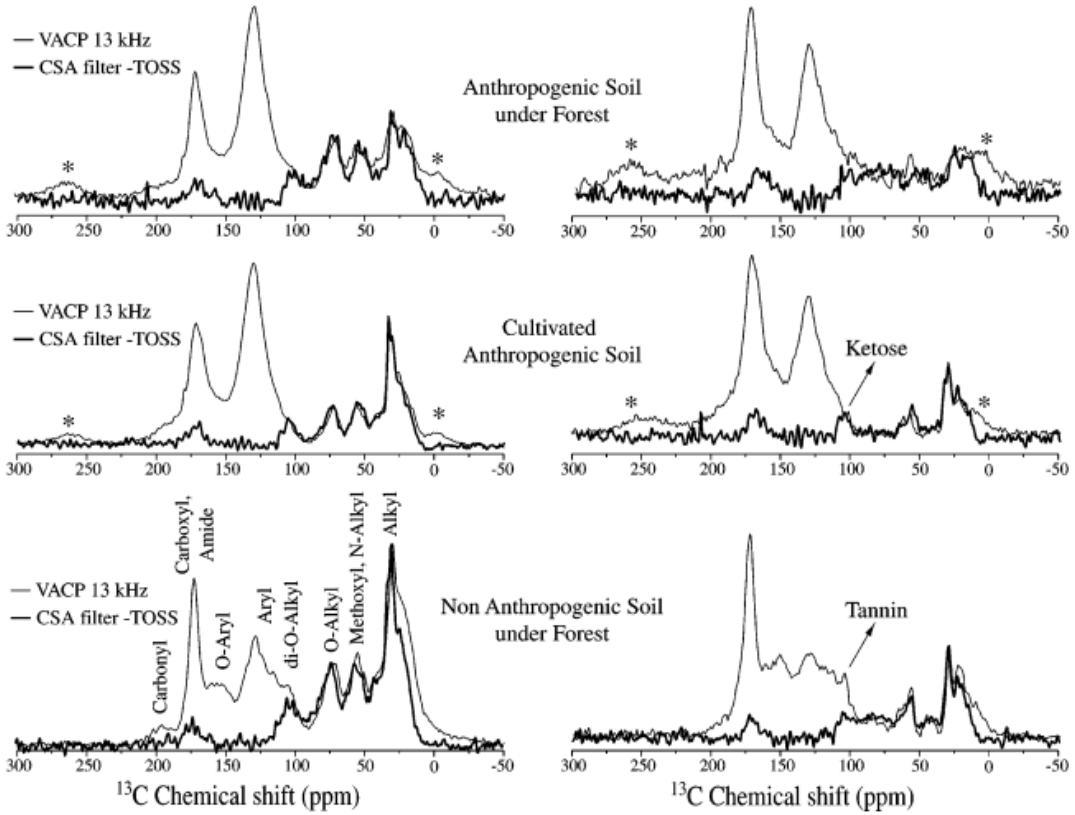


FIGURE 1. Left: Full VACP (13 kHz MAS) spectra of a humic acid sample extracted from Amazonian soils (thin line) and the corresponding VACP-TOSS spectrum (5 kHz MAS) after 35 μs CSA filter (thick line). Right: Corresponding VACP (13 kHz MAS) spectra after dipolar dephasing with 67 μs of gated decoupling (thin line) and corresponding VACP-TOSS spectrum (5 kHz MAS) after 35 μs CSA filter and 40 μs of gated decoupling (thick line). The symbols $*$ indicate the spinning sidebands.

Novotny et al., *Environ. Sci. Technol.* 2007;41:400-405

Biocarvões

RMN de ^{13}C:

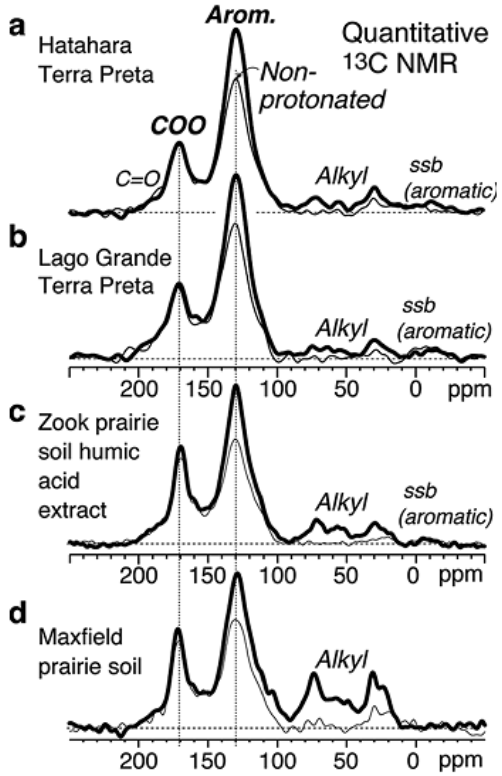


Figure 1. Quantitative, direct polarization ^{13}C NMR spectra of Terra Preta soil organic matter (HF-treated) from two sites (**a**) Hatahara and (**b**) Lago Grande. Thick line: spectrum of all carbons; thin line: spectrum of nonprotonated C and of CH_3. (**c**, **d**) Corresponding spectra of Iowa prairie soil organic matter: (**c**) humic acid extract of Zook soil and (**d**) unfractionated organic matter of Maxfield soil. The spectra were obtained at a resonance frequency of 100 MHz with 14-kHz magic-angle spinning. Spinning sidebands of the aromatic peaks are labeled "ssb (aromatic)" and were included in the tally of the total aromatic signal.

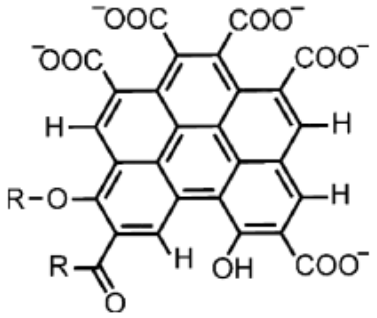


Figure 3. Model of a typical stable and fertile aromatic cluster in Terra Preta and temperate grassland soils, derived from NMR spectroscopy and H–C distance measurements.

Mao et al., *Environ. Sci. Technol.* 2012;46:9571-9576

Biocarvões

RMN de ^{13}C:

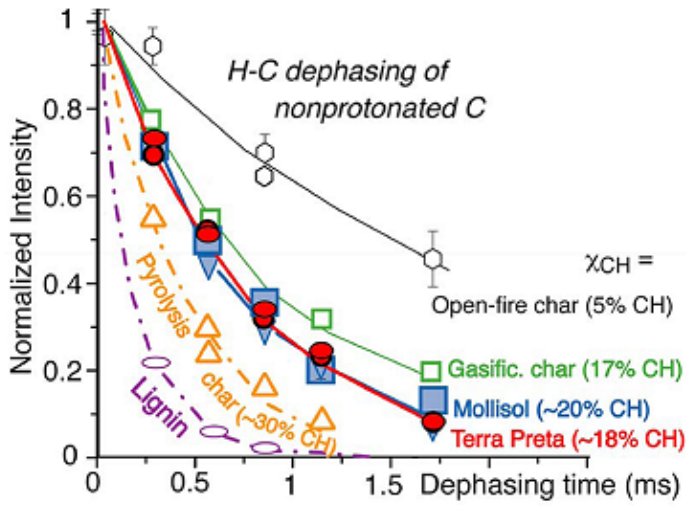


Figure 2. Size determination of aromatic clusters in Terra Preta soil organic matter (red filled ovals: Hatahara site; filled circles: Lago Grande site) as well as prairie-soil (Mollisol) humic acid extract (Zook, blue filled inverted triangles) and whole organic matter (Maxfield soil, blue filled squares) by long-range $^{1}H-^{13}C$ dipolar dephasing NMR. The normalized integral intensity of the nonprotonated aromatic carbon signal between 107 and 142 ppm is plotted as a function of the recoupled H−C dipolar dephasing time. For reference, data are also shown for open-fire grass char (open hexagons), gasification char (open squares), pyrolysis char (open triangles), and lignin (open ellipses) (from ref 20). The fraction of aromatic char carbons that are protonated is listed for each sample.

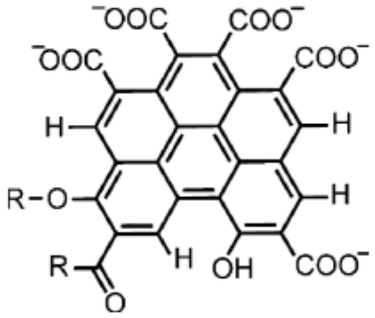


Figure 3. Model of a typical stable and fertile aromatic cluster in Terra Preta and temperate grassland soils, derived from NMR spectroscopy and H−C distance measurements.

Mao et al., *Environ. Sci. Technol.* 2012;46:9571-9576

Espécies adsorvidas em biocarvões

RMN de ^{13}C – benzeno adsorvido:

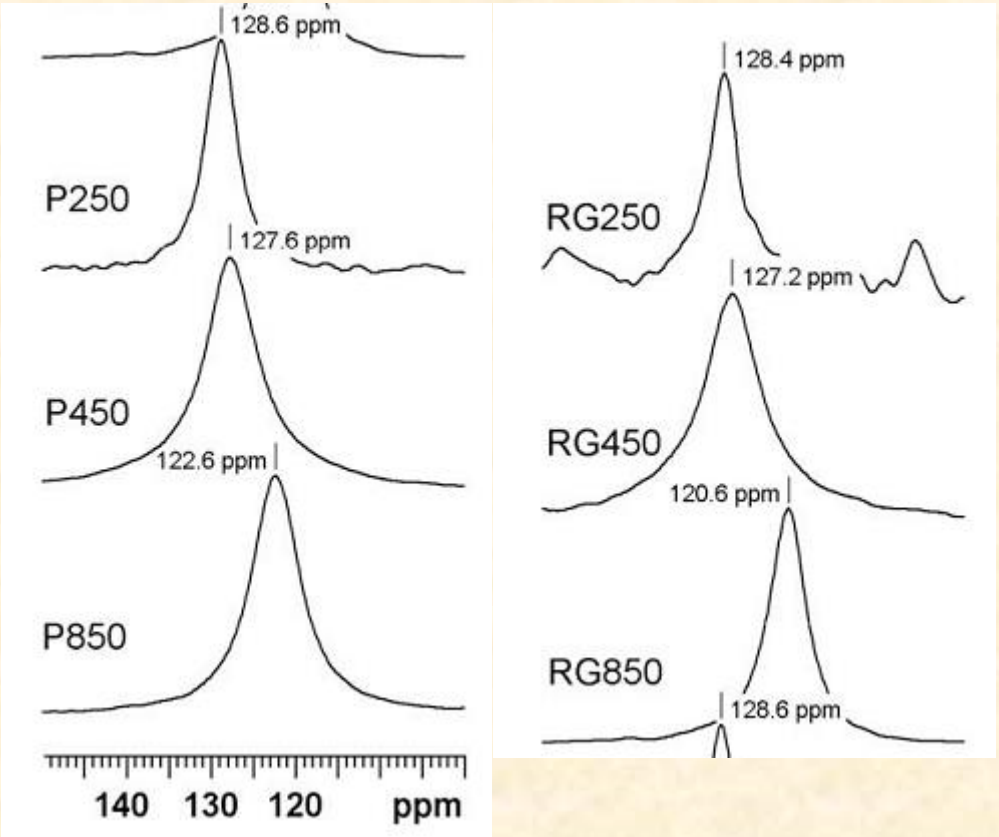


Fig. 4. Aromatic region of ^{13}C DP NMR spectra of heat-treated materials containing sorbed ^{13}C benzene.

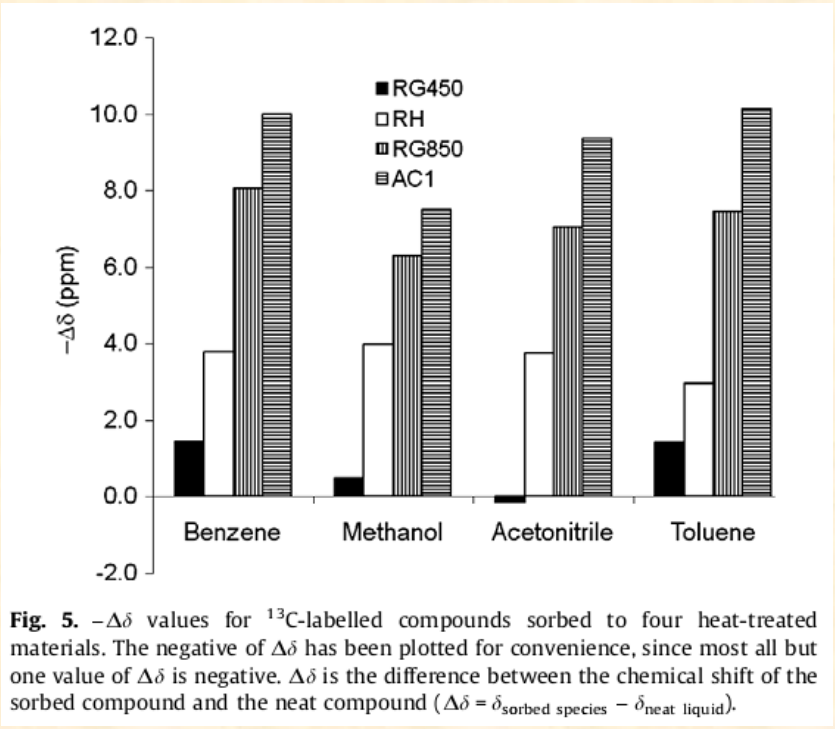
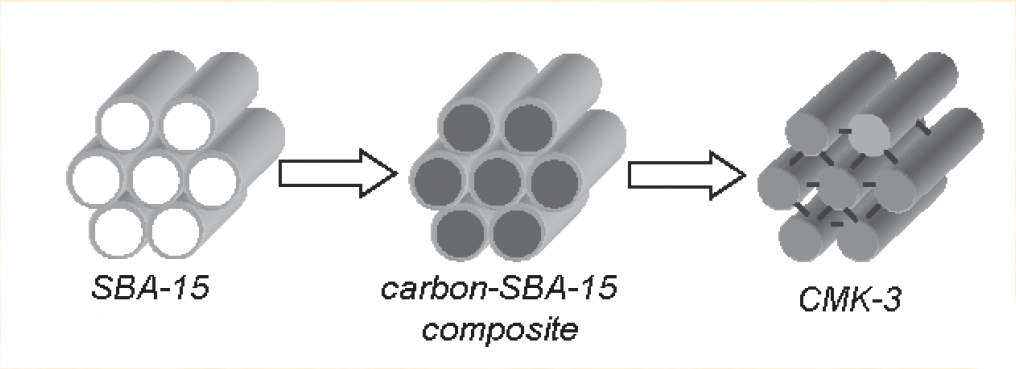


Fig. 5. $-\Delta\delta$ values for ^{13}C-labelled compounds sorbed to four heat-treated materials. The negative of $\Delta\delta$ has been plotted for convenience, since most all but one value of $\Delta\delta$ is negative. $\Delta\delta$ is the difference between the chemical shift of the sorbed compound and the neat compound ($\Delta\delta = \delta_{\text{sorbed species}} - \delta_{\text{neat liquid}}$).

McBeath & Smernik, *Org. Geochem.* 2009;40:1161-1168.

Outros materiais carbonosos porosos

Síntese de carbonos mesoporosos (CMK-3):



Pastore et al., *J. Braz. Chem. Soc.* 2006;17:16-29

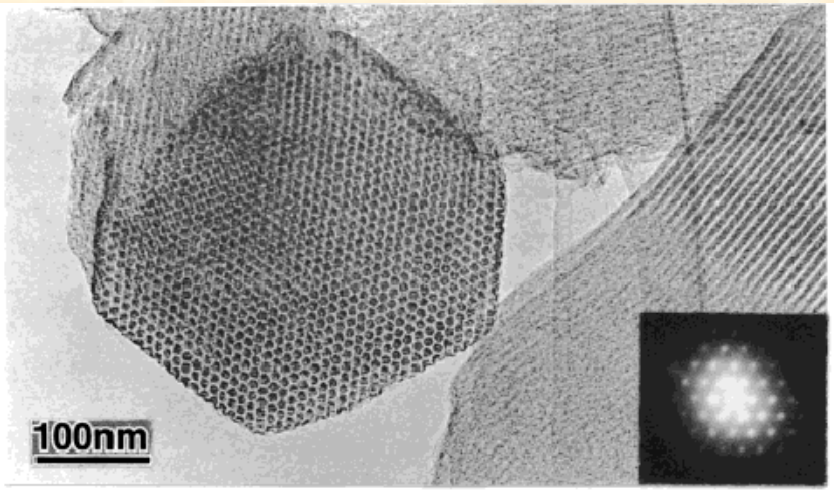


Figure 1. Typical TEM images of the ordered mesoporous carbon molecular sieve, CMK-3. This carbon was synthesized using sucrose as a carbon source and SBA-15 silica as a template. The TEM images were obtained with a JEM-4000 EX operated at 400 kV from the carbon material after silica template was completely removed with HF solution.

Jun et al., *J. Am. Chem. Soc.* 2000;122:10712-10713

Outros materiais carbonosos porosos

Estrutura de carbonos mesoporosos (CMK-3):

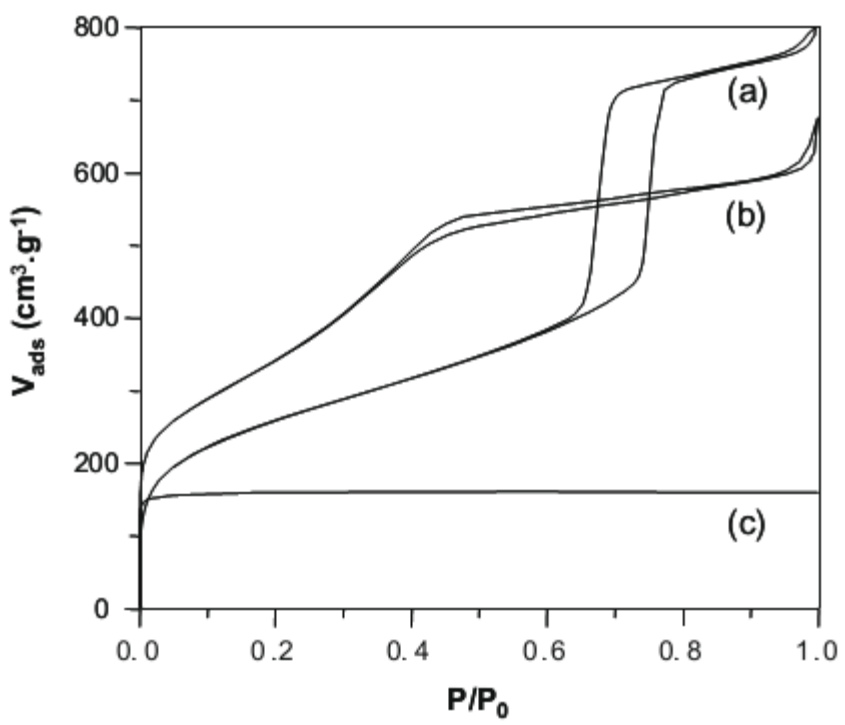


Fig. 2 – Nitrogen adsorption/desorption isotherm of SBA-15 (a), CMK-3 (b) and C-micro (c).

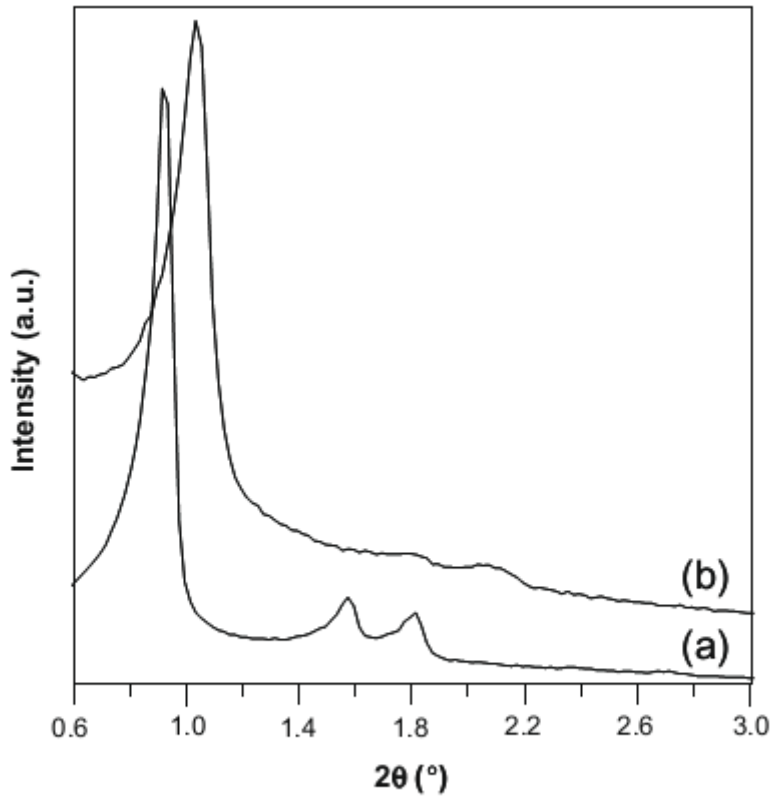


Fig. 1 – XRD pattern of SBA-15 (a) and CMK-3 (b).

Onfroy et al., *Carbon* 2009;47:2352-2357

Outros materiais carbonosos porosos

RMN de ^{129}Xe em carbonos mesoporosos (CMK-3):

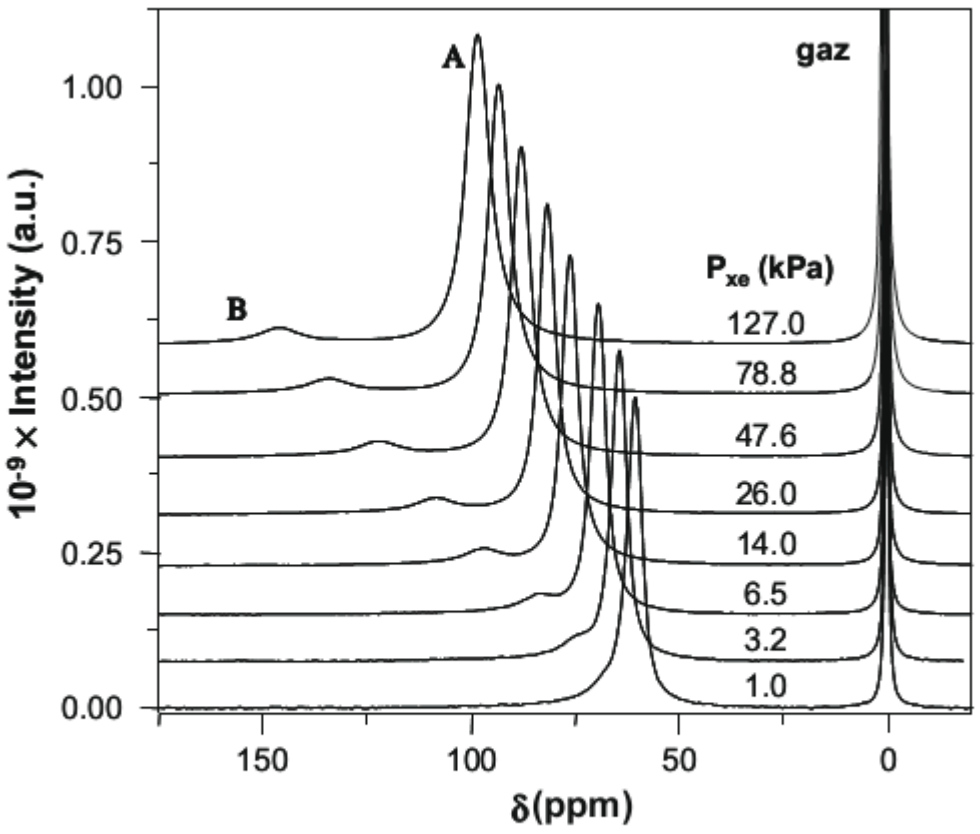


Fig. 3 – Influence of the Xe pressure on NMR spectra of optically polarized ^{129}Xe in CMK-3.

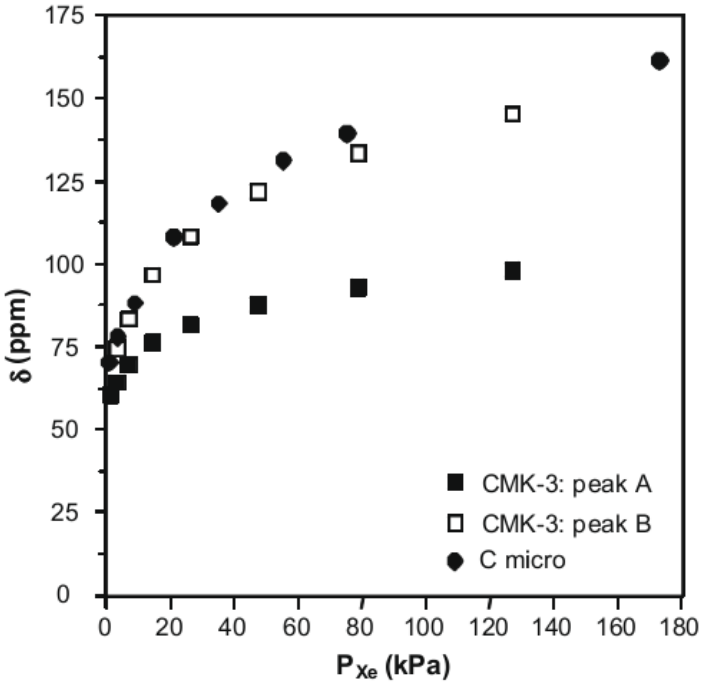


Fig. 4 – ^{129}Xe NMR chemical shift of Xe adsorbed on CMK-3 (■ and □) and C-micro (●) at room temperature.

Onfroy et al., *Carbon* 2009;47:2352-2357

Outros materiais carbonosos porosos

RMN de ^{129}Xe em carbonos mesoporosos (CMK-3) – 2D Exchange:

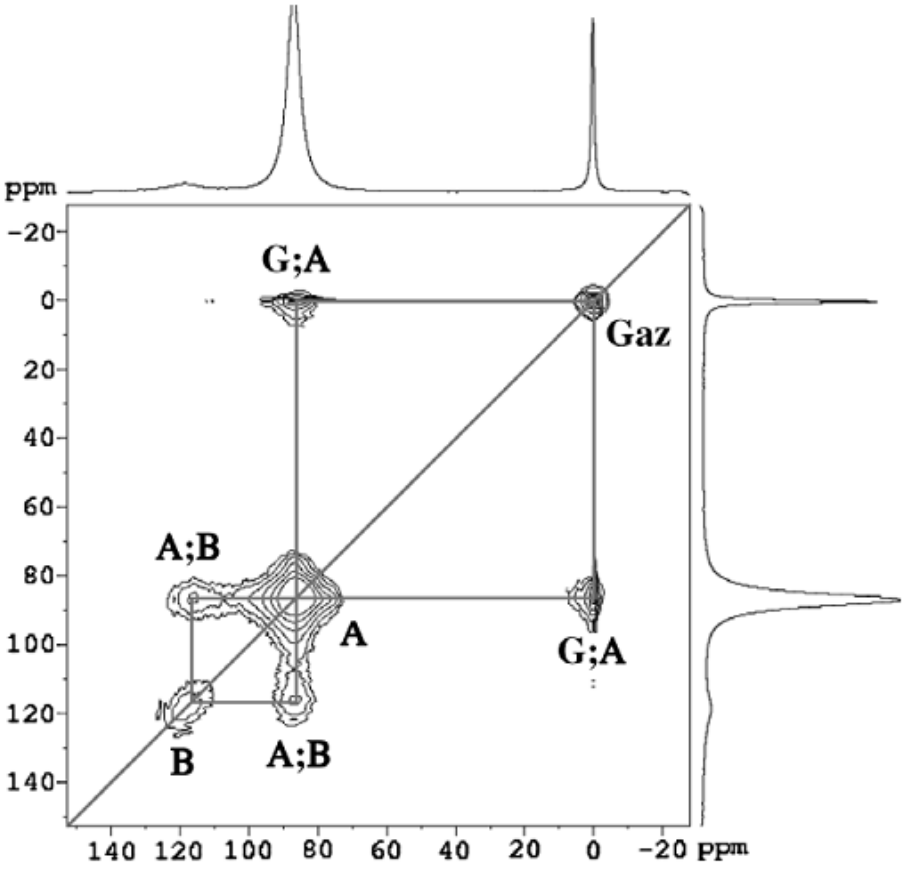
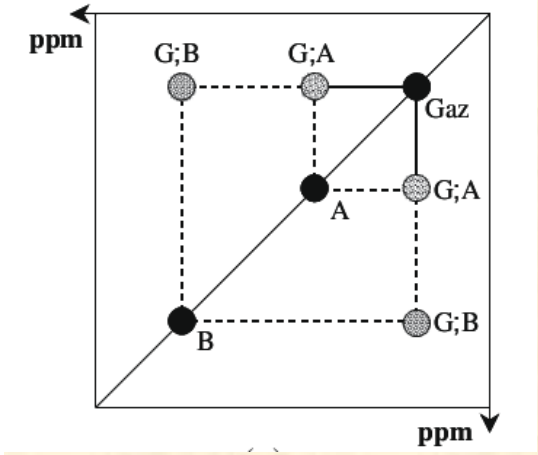
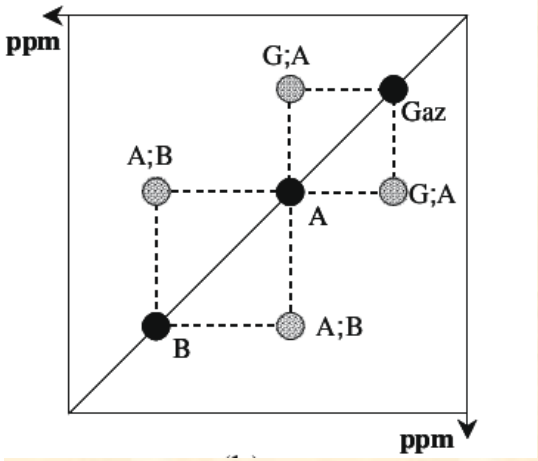


Fig. 6 – ^{129}Xe 2D-EXSY map obtained on CMK-3 at 295 K (P_{Xe} = 53 kPa; mixing time = 50 ms).



Micro e mesoporos separados

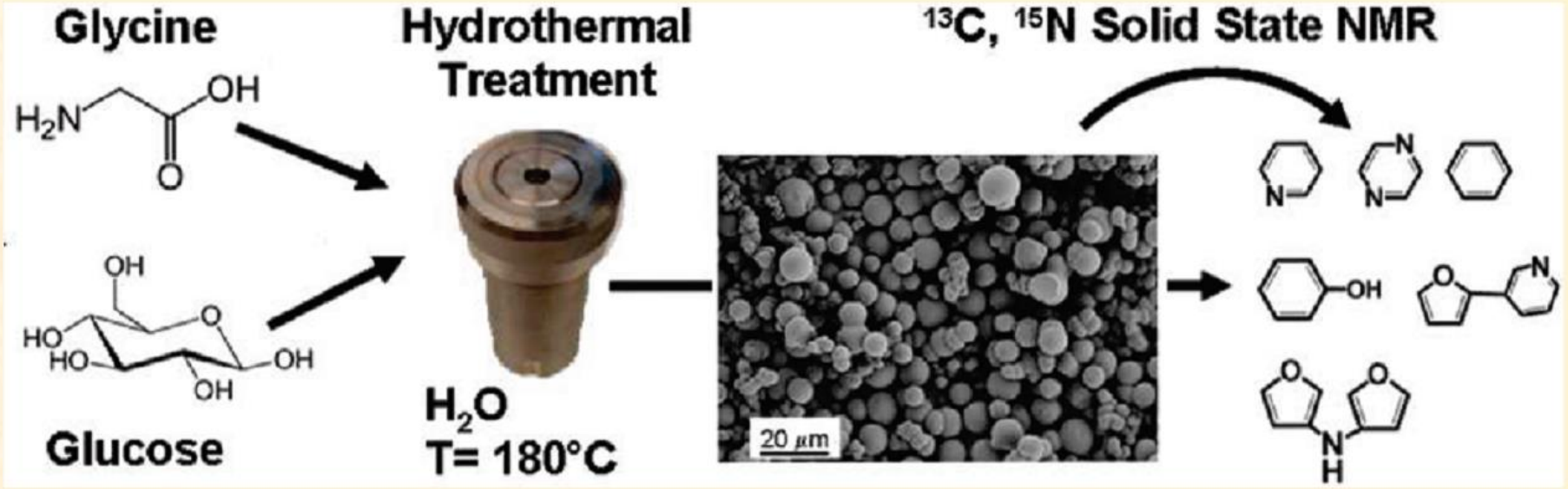


Micro e mesoporos interconectados

Onfroy et al., *Carbon* 2009;47:2352-2357

Carbonos hidrotérmicos

Síntese de carbonos hidrotérmicos:



Baccile et al., *J. Phys. Chem. C* 2011;115:8976-8982

Carbonos hidrotérmicos

Morfologia – microesferas de carbono:

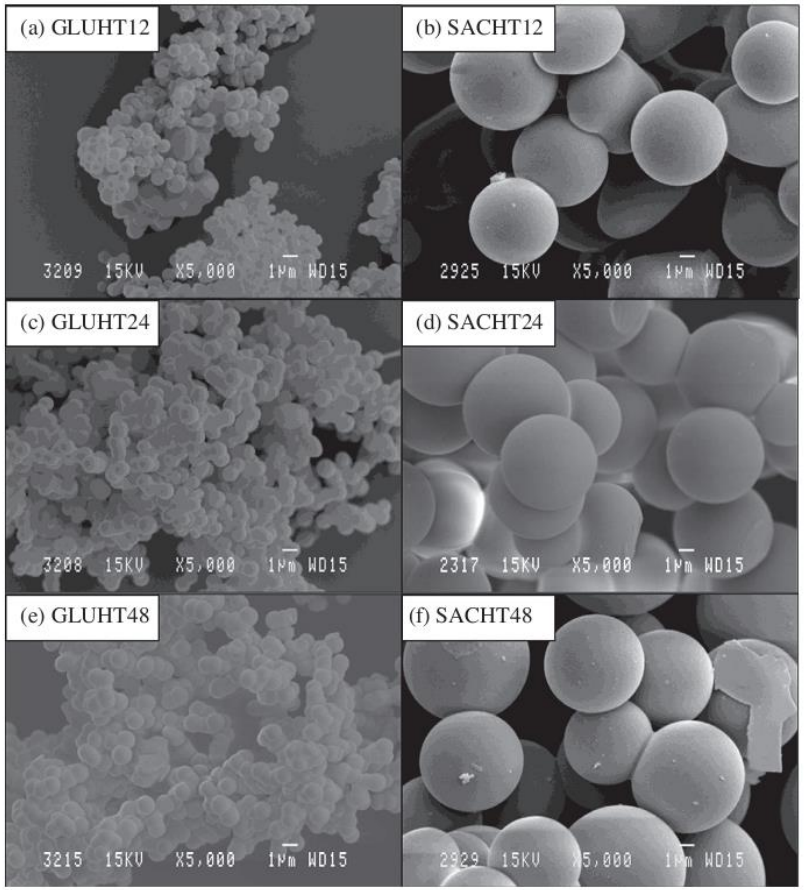


Fig. 2 – SEM images of the spherical carbons obtained by hydrothermal treatment of GLU and SAC at different times: (a) and (b) at 12 h, (c) and (d) at 24 h, (e) and (f) at 48 h.

Romero-Anaya et al., *Carbon* 2014;68:296-307

Carbonos hidrotérmicos

RMN de ^{13}C / ^{15}N – materiais isotopicamente enriquecidos:

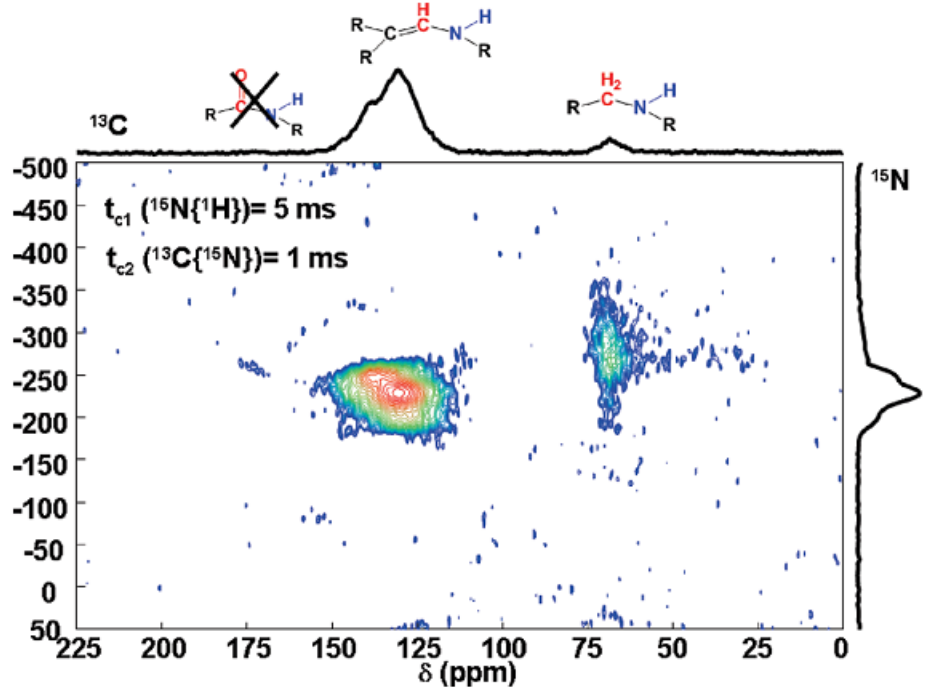
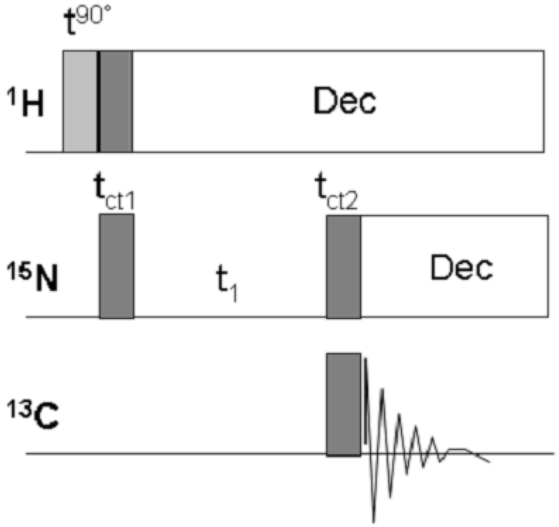


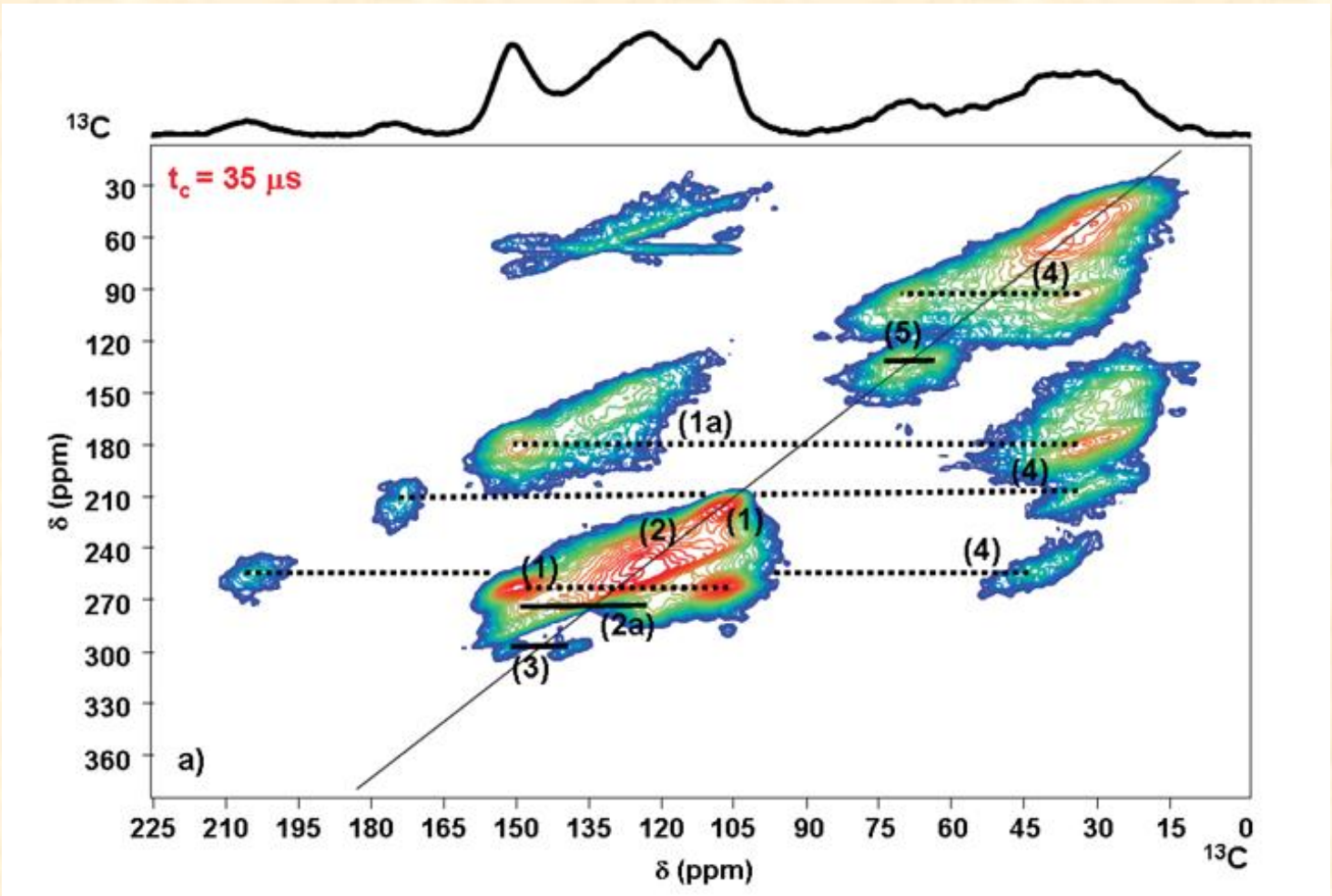
Figure 4. 2D map showing the double CP $^{13}C\{^{1}H, ^{15}N\}$ experiment on the HC glu-C13-N15-gly system and obtained with pulse sequence shown in Figure 1 in the Supporting Information. Contact times for each CP step are given in the figure. Insight on the possible chemical groups is reported in Figure 5. Note that here "R" is just a general notation to refer to C or H elements.

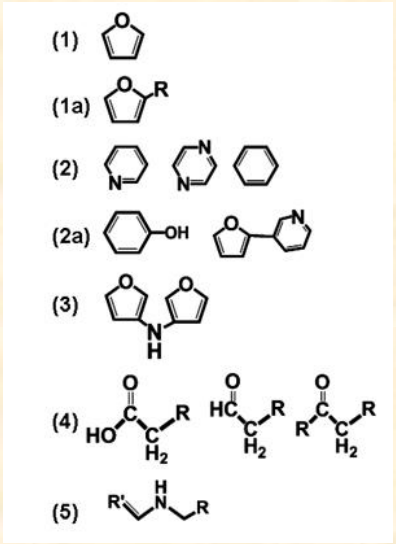


Baccile et al., *J. Phys. Chem. C* 2011;115:8976-8982

Carbonos hidrotérmicos

RMN de ^{13}C SQ-DQ – materiais isotopicamente enriquecidos:





Baccile et al., *J. Phys. Chem. C* 2011;115:8976-8982

Estudos de óxido de grafeno

Síntese de óxido de grafite / óxido de grafeno:

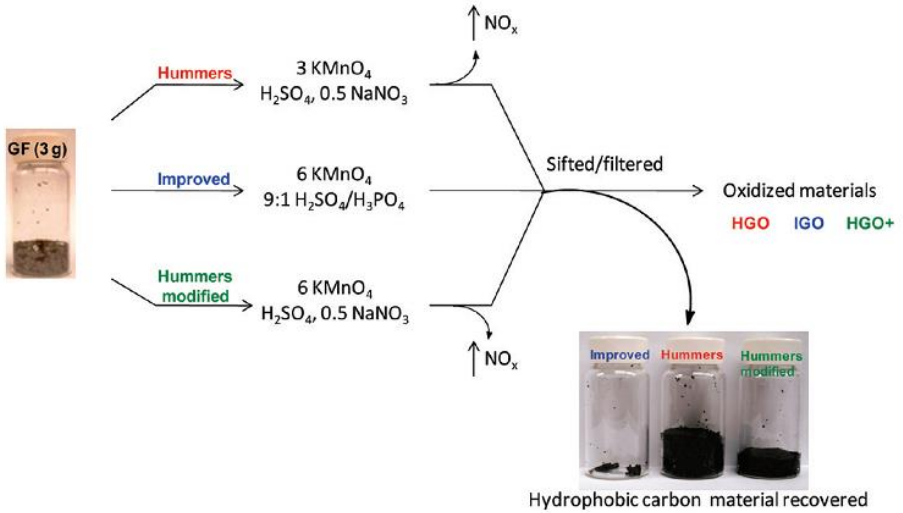


Figure 1. Representation of the procedures followed starting with graphite flakes (GF). Under-oxidized hydrophobic carbon material recovered during the purification of IGO, HGO, and HGO+. The increased efficiency of the IGO method is indicated by the very small amount of under-oxidized material produced.

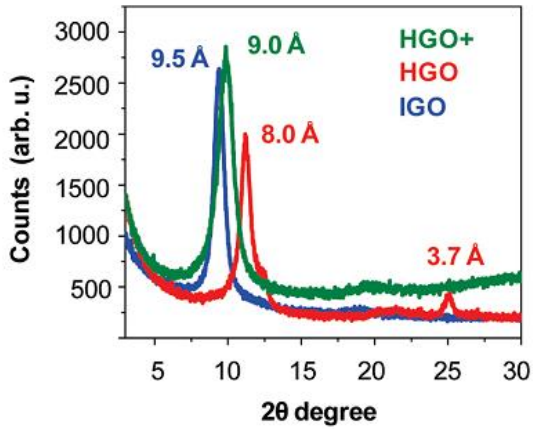


Figure 6. XRD spectra of HGO, HGO+, and IGO (1.54059 Å Cu Kα 1 as wavelength).

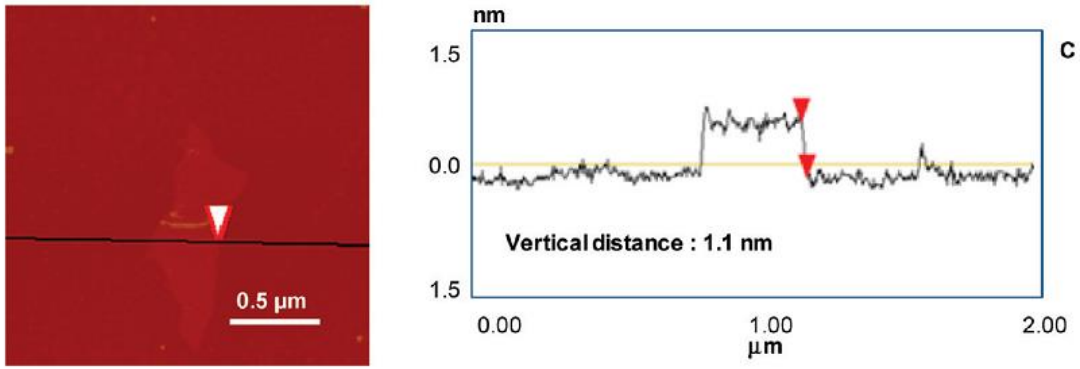
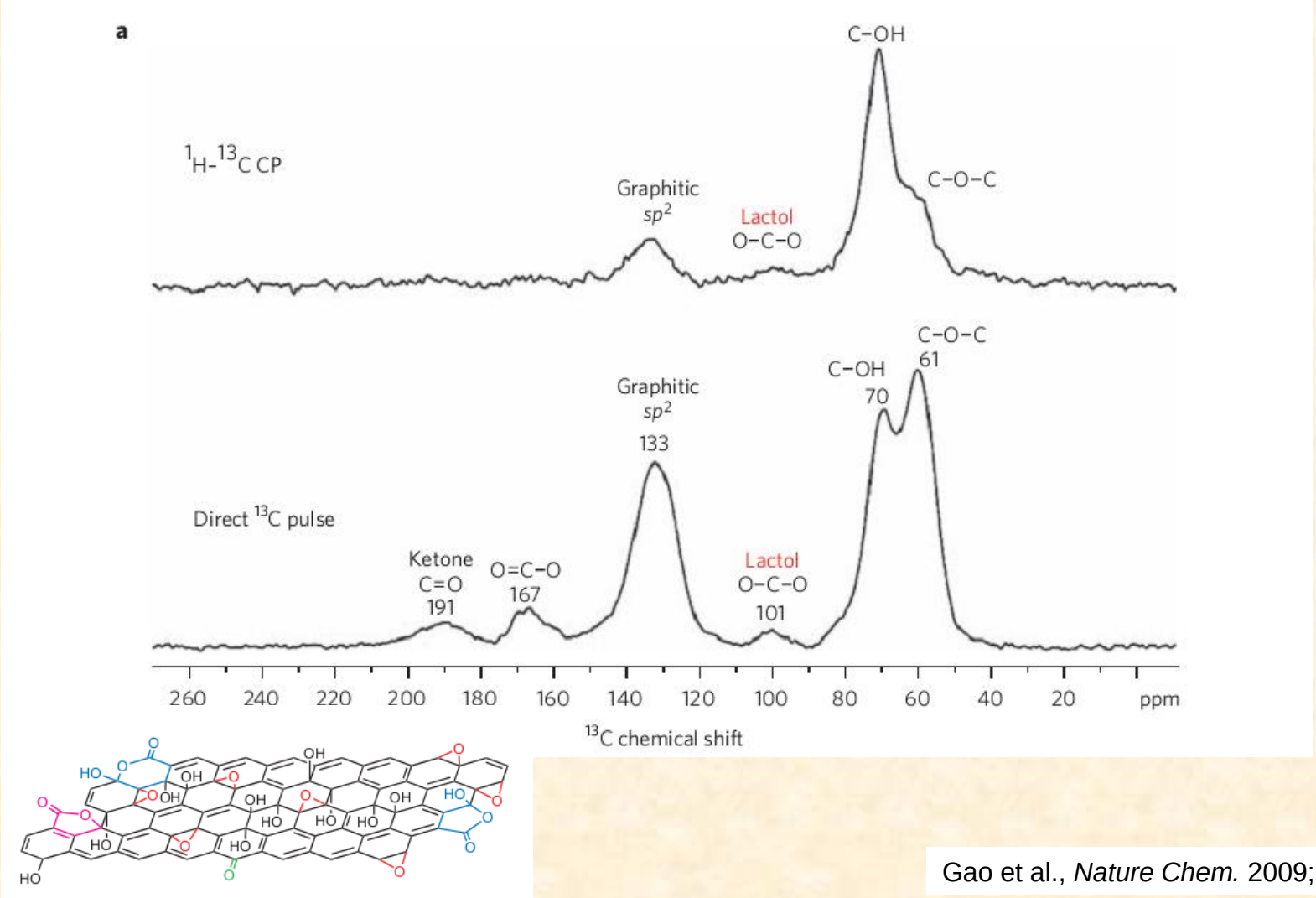


Figure 3. Tapping mode AFM topographic images and height profiles of a single layer of (A) HGO+, (B) HGO, and (C) IGO.

Marcano et al., *ACS Nano* 2010;4:4806

Estudos de óxido de grafeno

RMN de ^{13}C:



Gao et al., *Nature Chem.* 2009;1:403-408

Estudos de óxido de grafeno

Modelos estruturais:

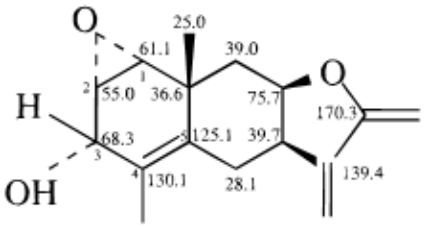


Figure 6. Model compound for the assignment of the ^{13}C NMR spectra of GO. Carbons 1 and 2, carbon 3 and carbons 4 and 5 correspond to C−O−C, C−OH, and double bonds in the structure of GO, respectively.

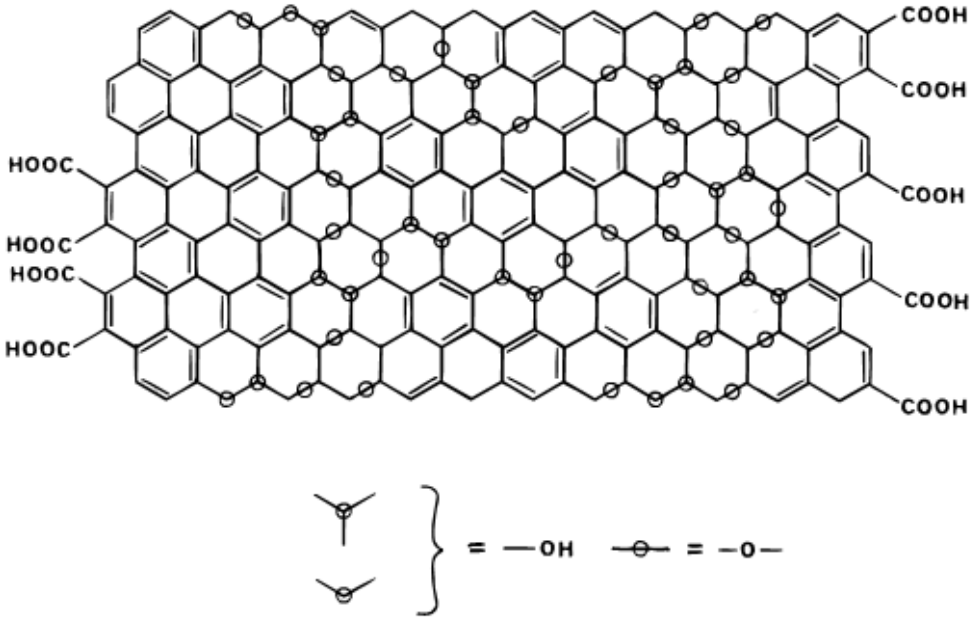


Figure 7. New structural model of GO.

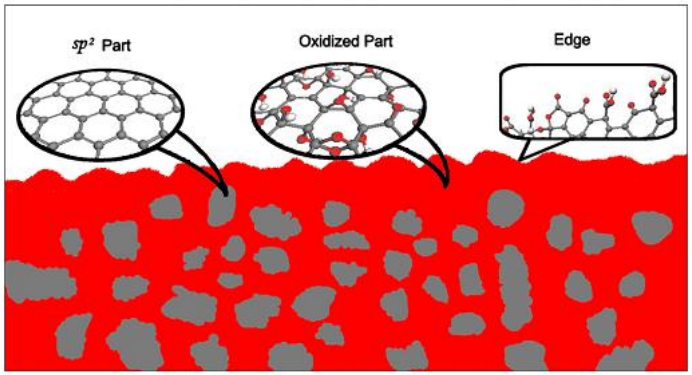


FIG. 6. A schematic GO atomic structure.

Lu et al., *J. Phys. Chem. C* 2010;133:034502

Lerf et al., *J. Phys. Chem. B* 1998;102:4477-4482

Estudos de óxido de grafeno

RMN de ^{13}C – materiais com enriquecimento isotópico:

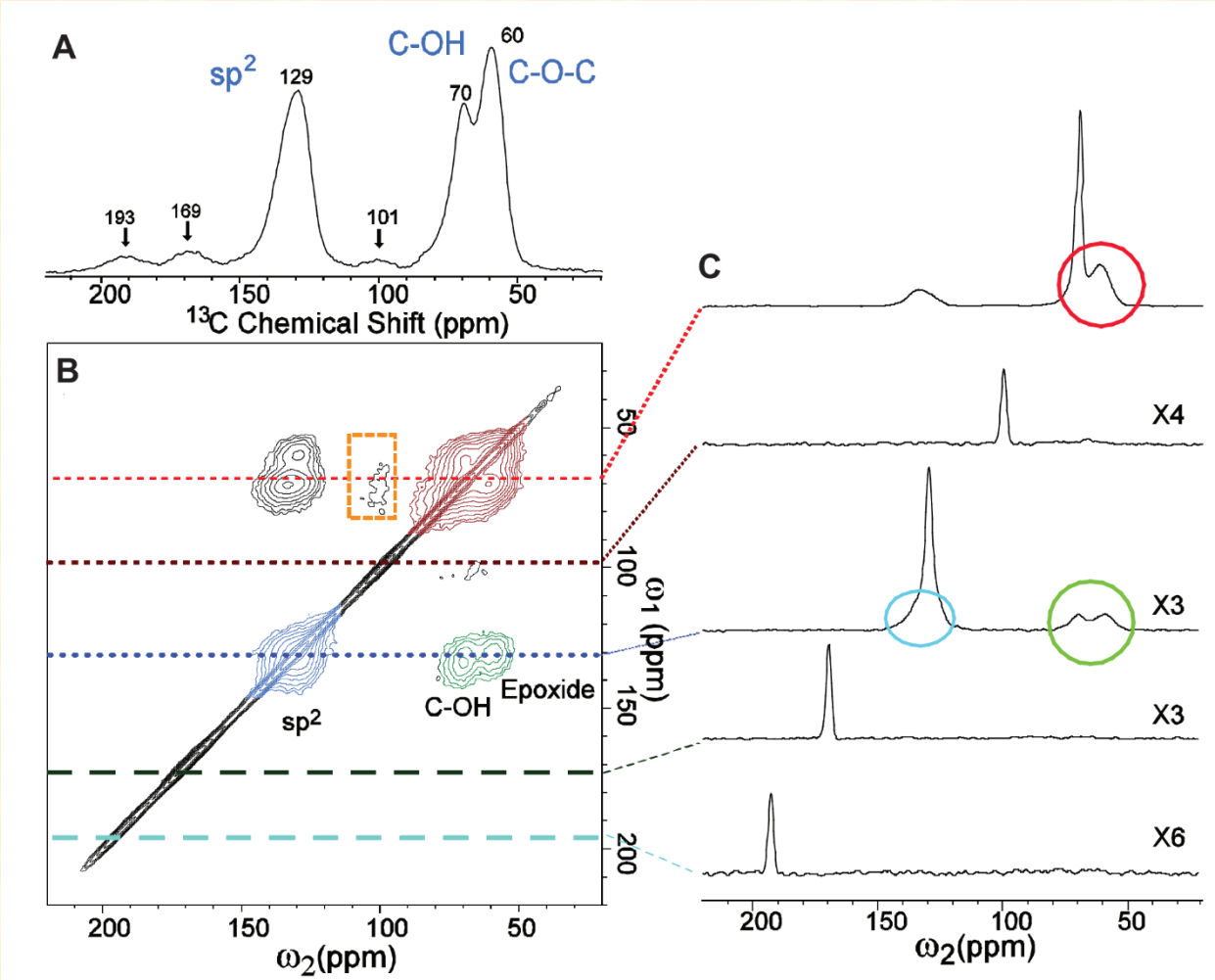
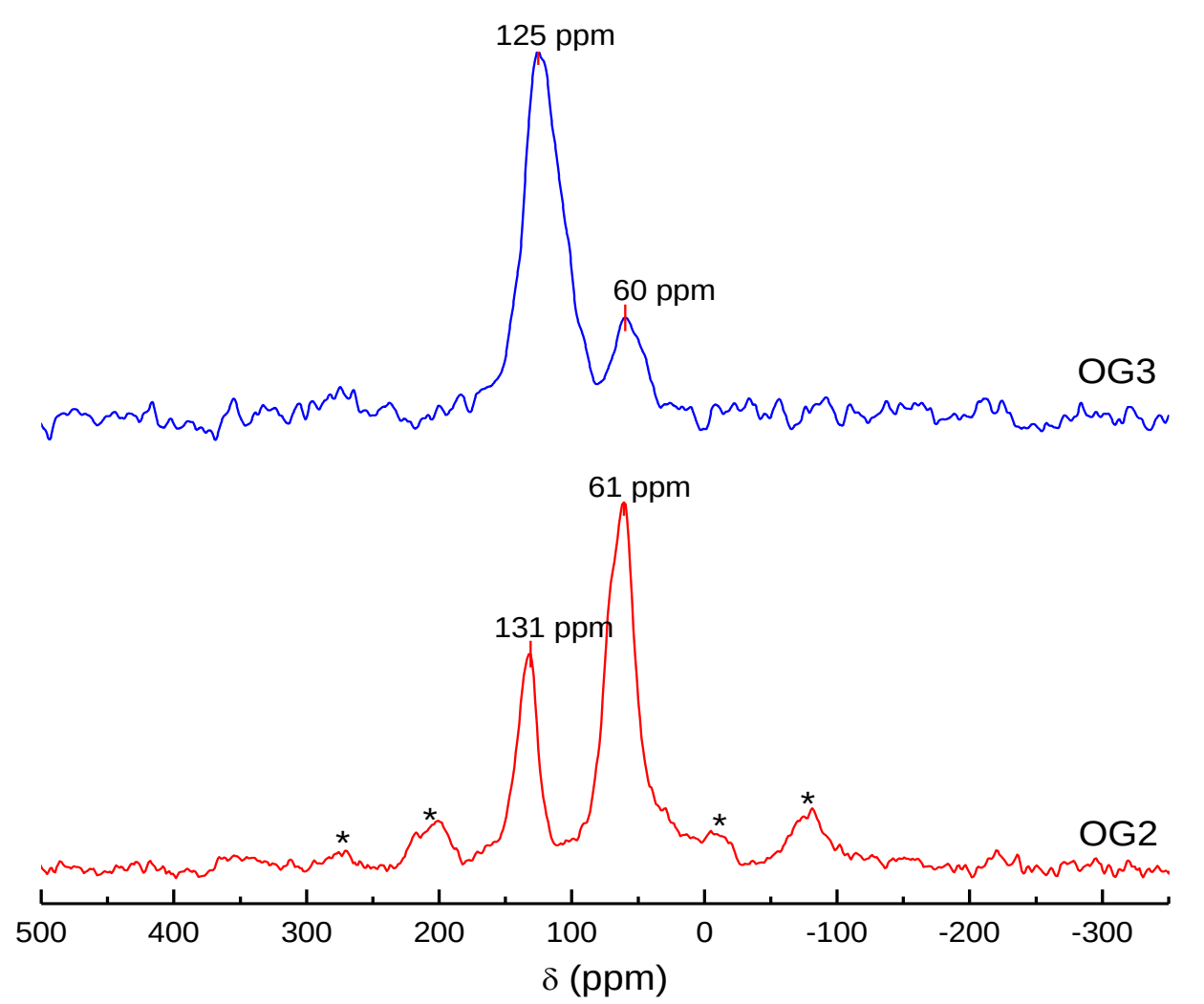


Fig. 3 (**A**) 1D ^{13}C MAS and (**B**) 2D $^{13}C/^{13}C$ chemical-shift correlation solid-state NMR spectra of ^{13}C-labeled graphite oxide with (**C**) slices selected from the 2D spectrum at the indicated positions (70, 101, 130, 169, and 193 ppm) in the ω_1 dimension. All the spectra were obtained at a ^{13}C NMR frequency of 100.643 MHz with 90 kHz ^{1}H decoupling and 20 kHz MAS for 12 mg of the sample. In (A), the ^{13}C MAS spectrum was obtained with direct ^{13}C excitation by a $\pi/2$-pulse. The recycle delay was 180 s, and the experimental time was 96 min for 32 scans. In (B), the 2D spectrum was obtained with cross polarization and fpRFDR ^{13}C-^{13}C dipolar recoupling sequence (*24*). The experimental time is 12.9 hours with recycle delays of 1.5 s and 64 scans for each real or imaginary t_1 point. A Gaussian broadening of 150 Hz was applied. The green, red, and blue areas in (B) and circles in (C) represent cross peaks between sp^2 and C-OH/epoxide (green), those between C-OH and epoxide (red), and those within sp^2 groups (blue), respectively.

Cai et al., *Science* 2008;321:1815

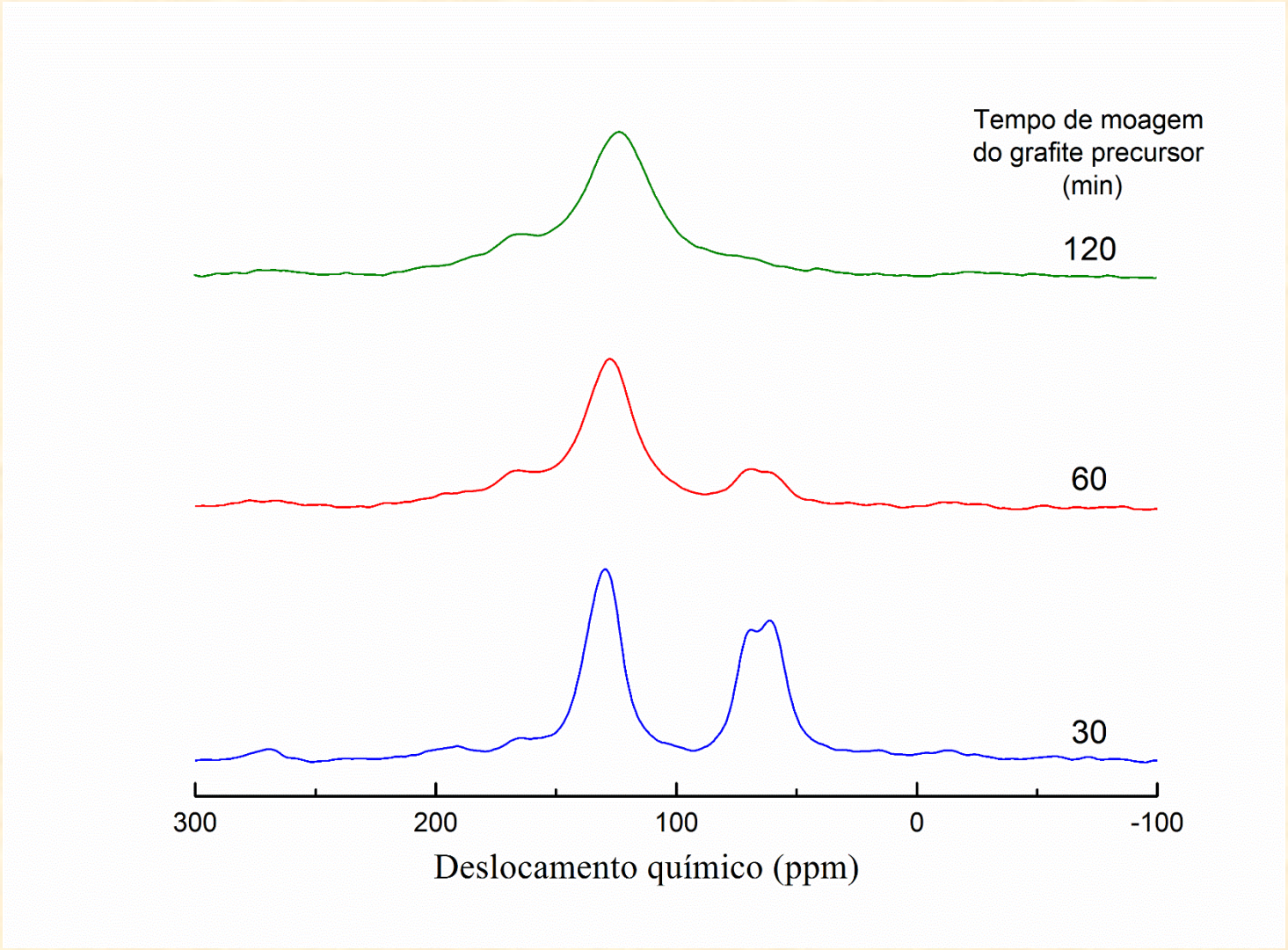
Estudos de óxido de grafeno

RMN de ^{13}C – materiais sintetizados a partir de diferentes grafites:



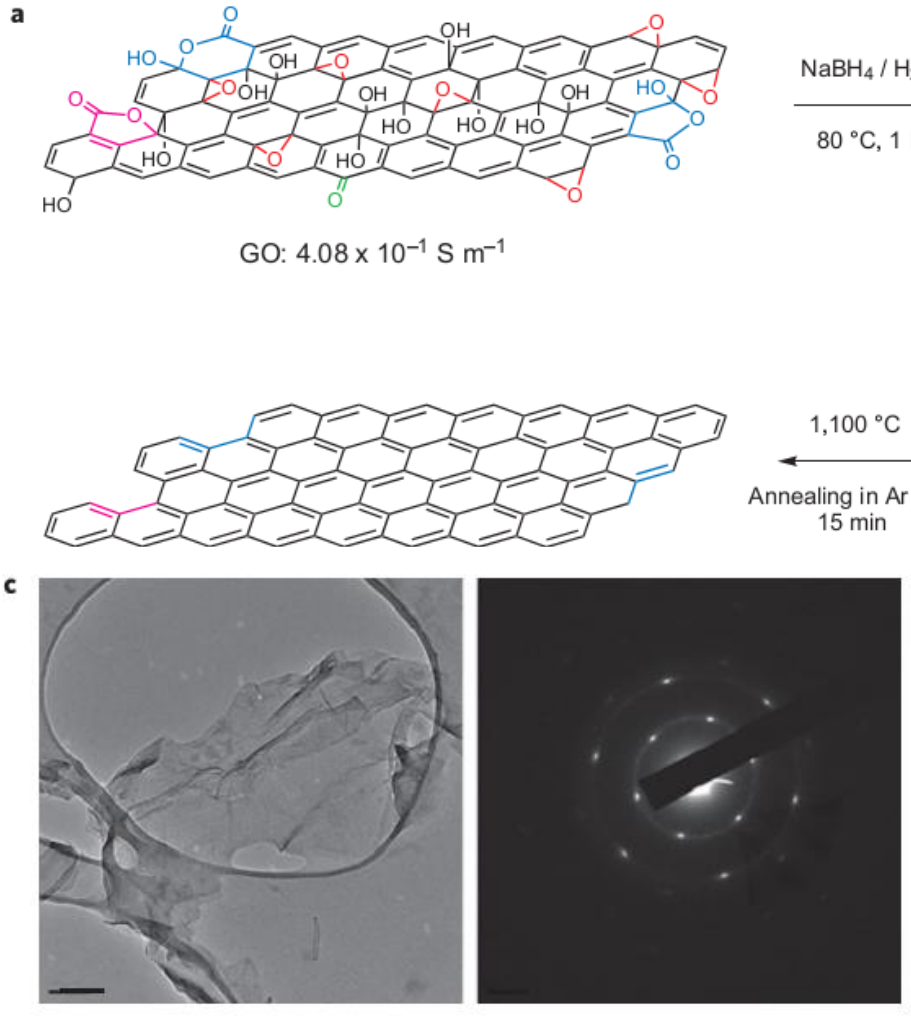
Estudos de óxido de grafeno

RMN de ^{13}C – materiais sintetizados a partir de diferentes grafites:



Estudos de óxido de grafeno

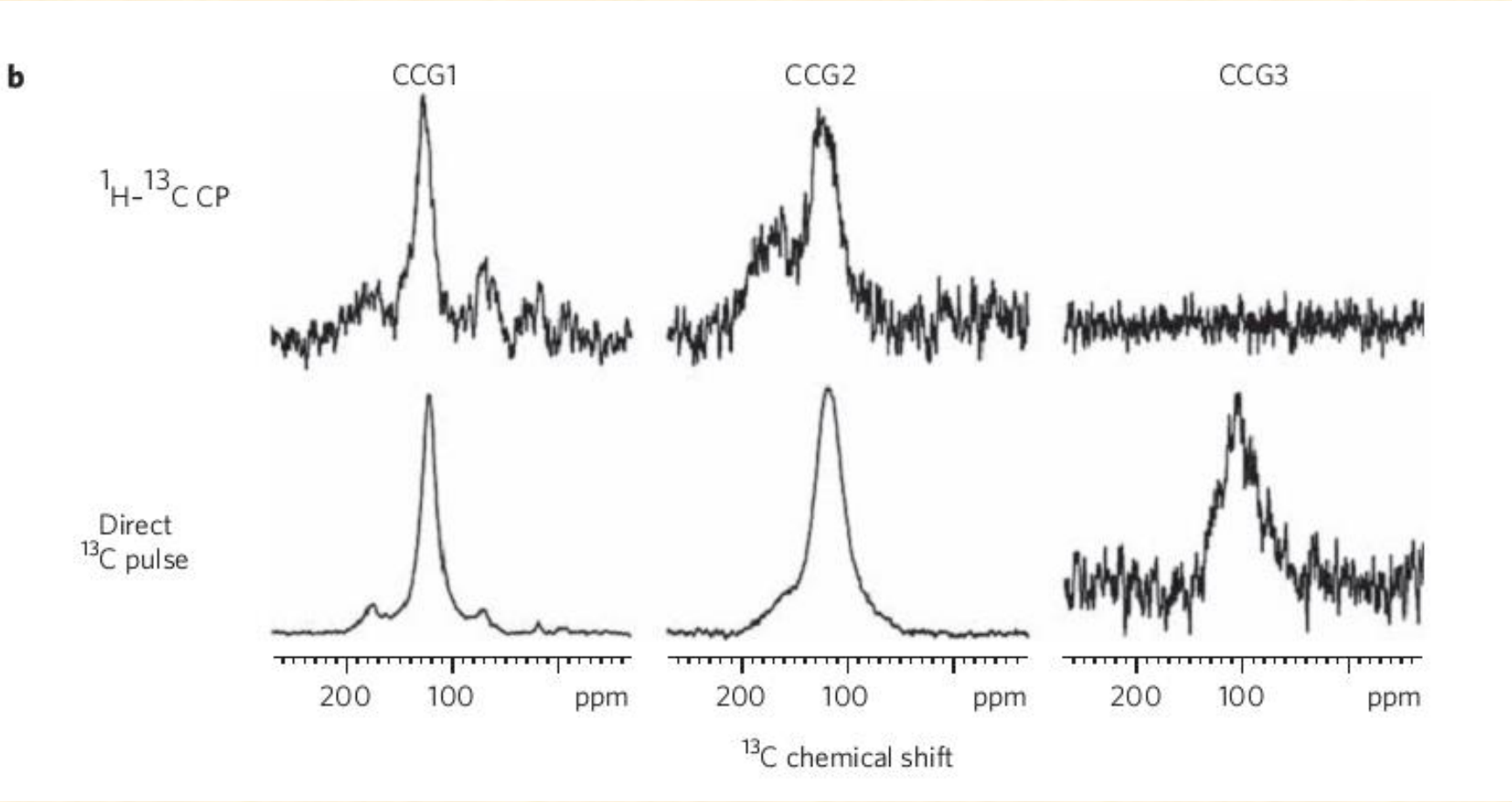
Síntese de grafeno – redução do óxido de grafeno:



Gao et al., *Nature Chem.* 2009;1:403-408

Estudos de óxido de grafeno

Síntese de grafeno – redução do óxido de grafeno:



Gao et al., *Nature Chem.* 2009;1:403-408

Estudos de óxido de grafeno

Síntese de grafeno – redução do óxido de grafeno:

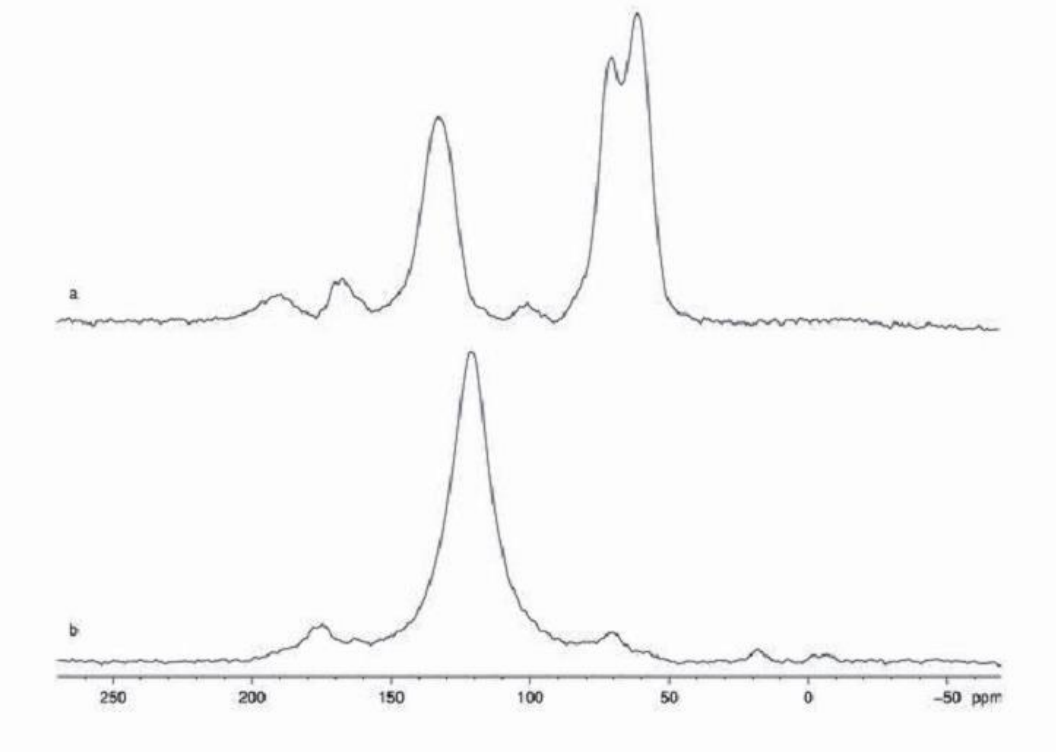


Figure S8. **Effect of $NaBH_4$ treatment on GO.** (a) Expanded plot of Figure 2a, direct ^{13}C pulse spectrum of GO. (b) Expanded plot of Figure 2b, direct ^{13}C pulse spectrum of CCG1

Gao et al., *Nature Chem.* 2009;1:403-408

Magnetismo em grafeno com vacâncias

Vacâncias isoladas:

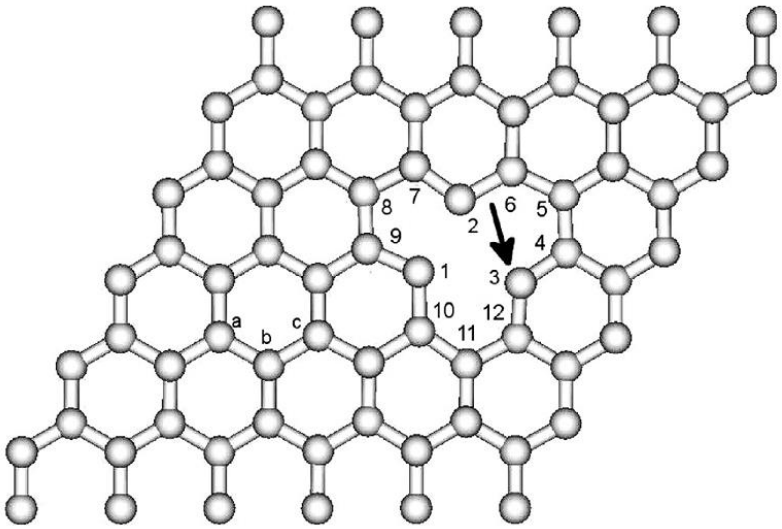


Fig. 1. The relaxed atomic structure of the graphene sheet with a single vacancy, where spheres represent the carbon atoms. The arrow indicates the atom 3 with the dangling σ bond and atoms 1 and 2 are those rebonded.

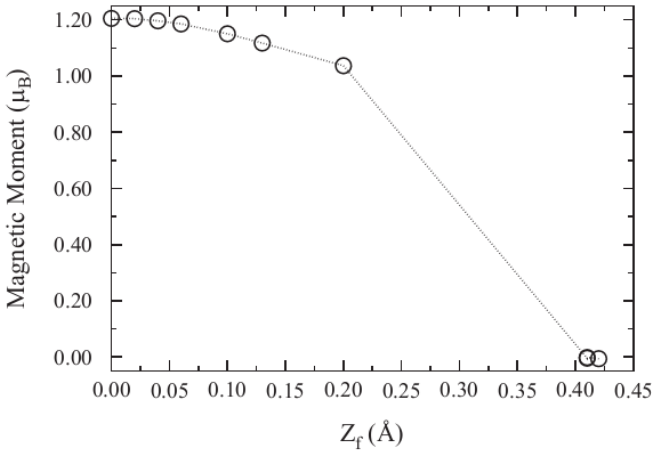
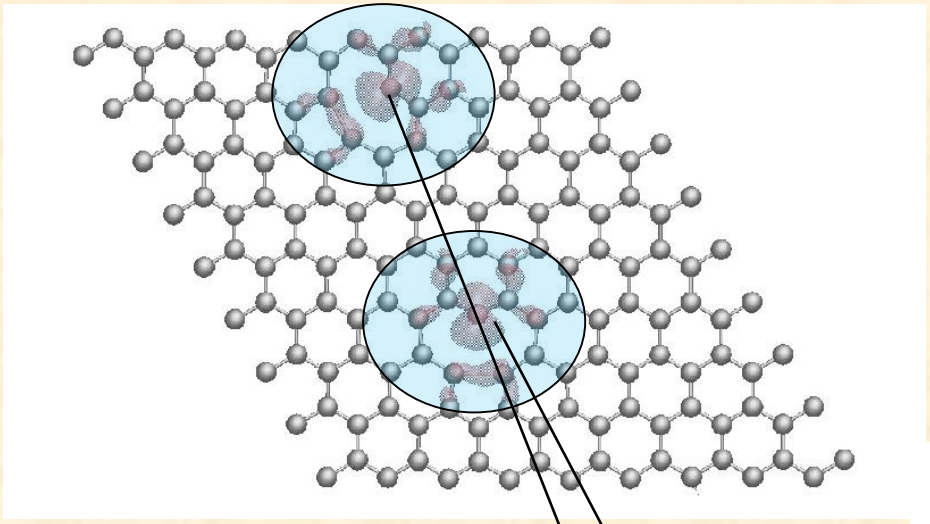


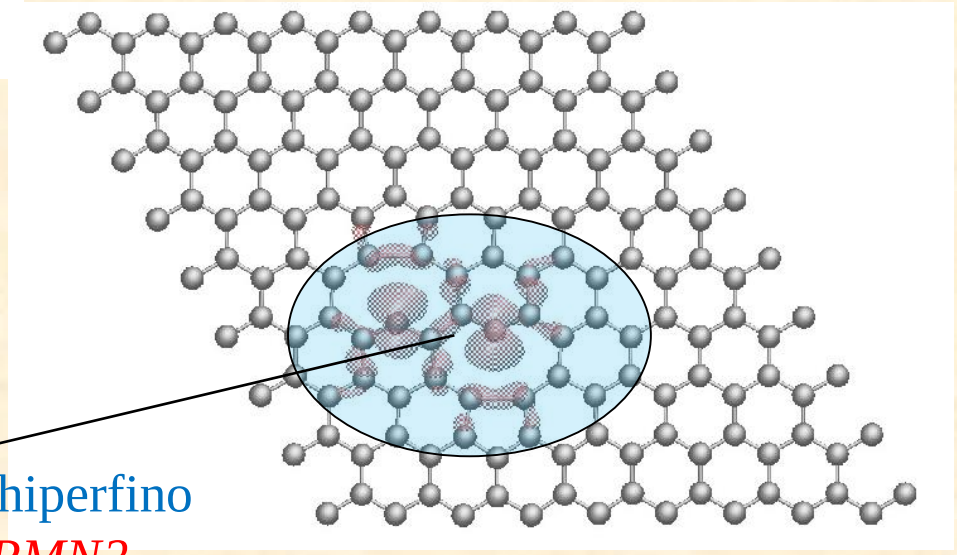
Fig. 3. Magnetic moment of the graphene sheet containing a single vacancy calculated as a function of the displacement of atom 3 perpendicular to the sheet for the relaxed structure. The line connecting the points is a guide for the eyes.

W.S. Paz et al. / Solid State Communications 175-176 (2013) 71–75

Magnetismo em grafeno com vacâncias

Vacâncias múltiplas:



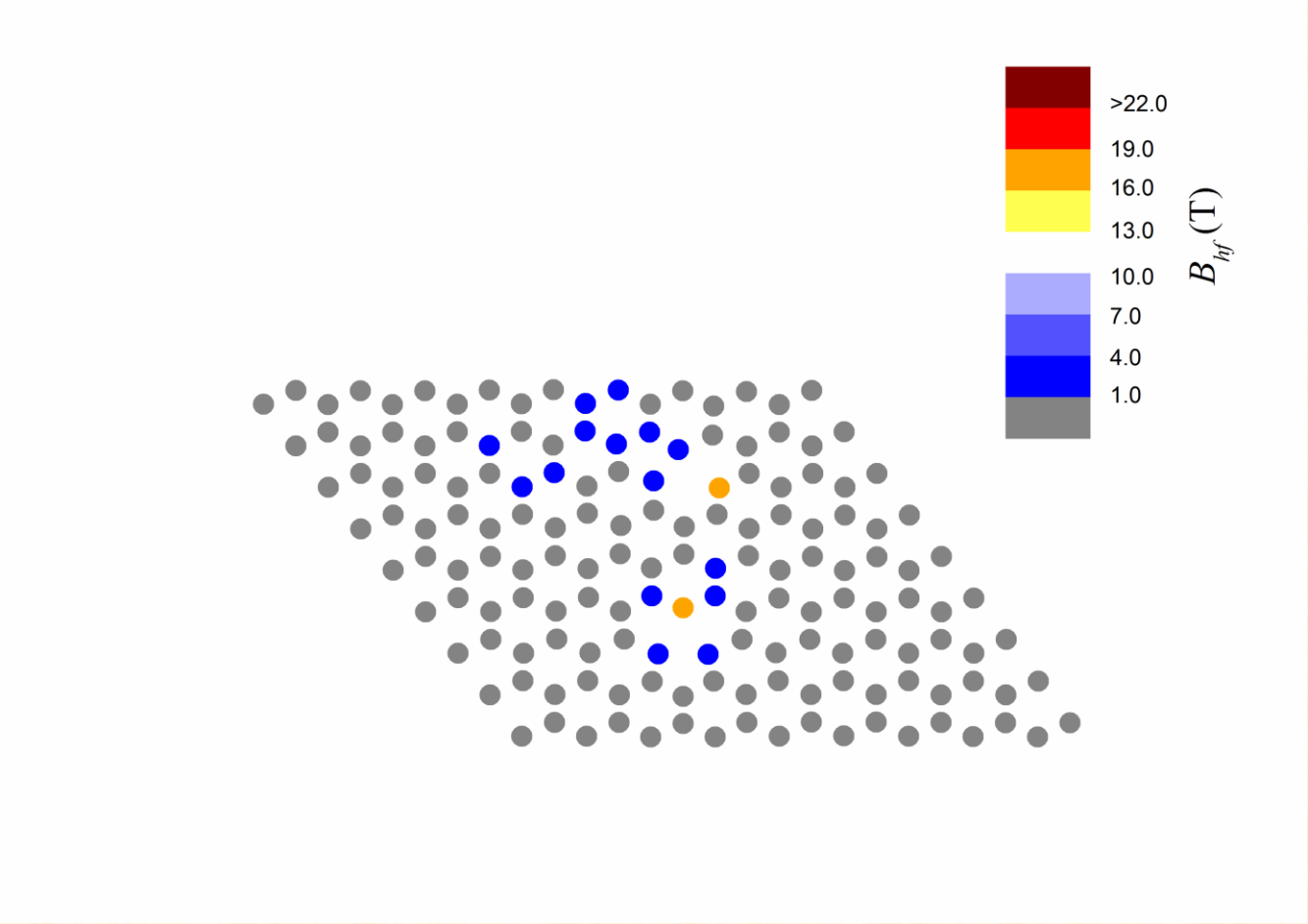


Campo magnético hiperfino

Detectável por RMN?

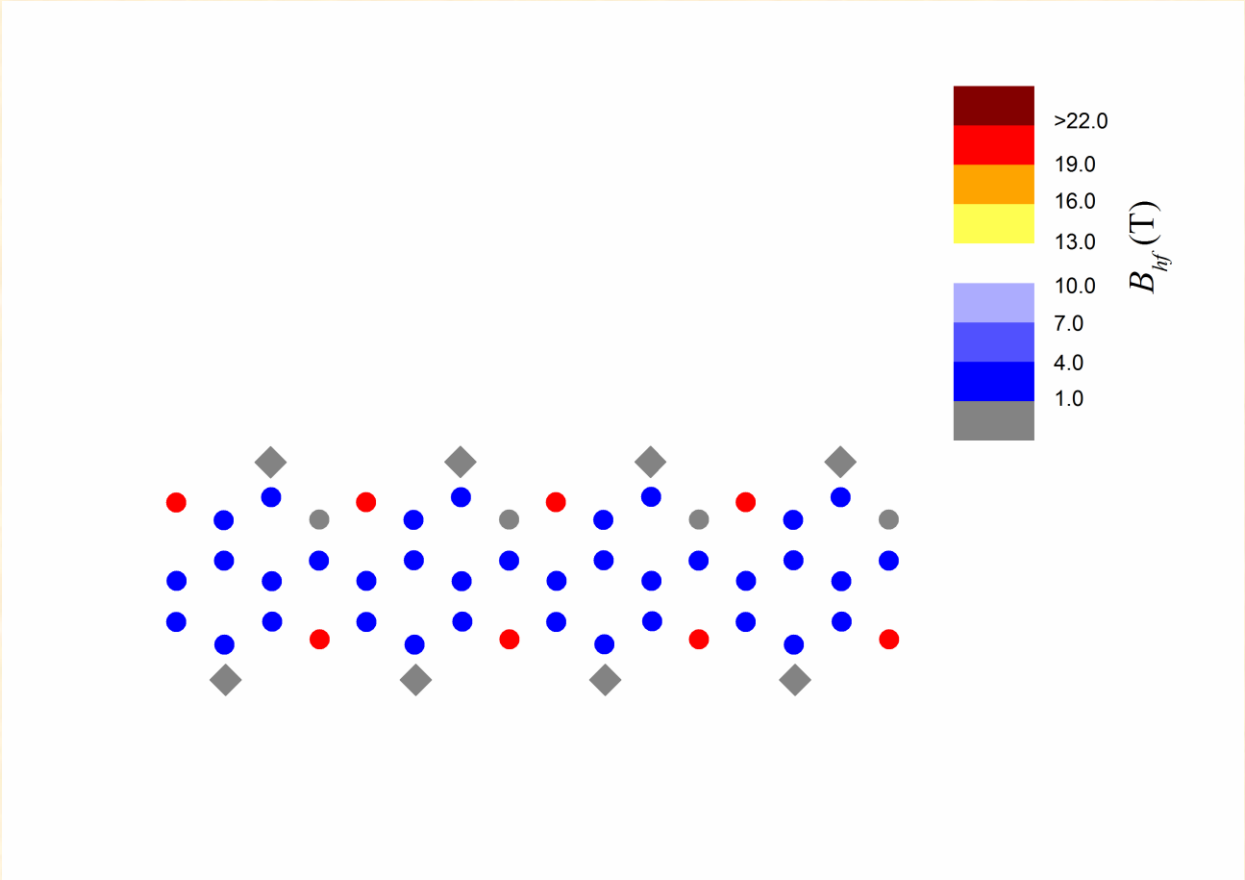
Magnetismo em grafeno com vacâncias

Cálculo DFT do campo magnético hiperfino (B_{hf}) nos sítios de carbono:



Magnetismo em grafeno com vacâncias

Cálculo DFT do campo magnético hiperfino (B_{hf}) nos sítios de carbono:



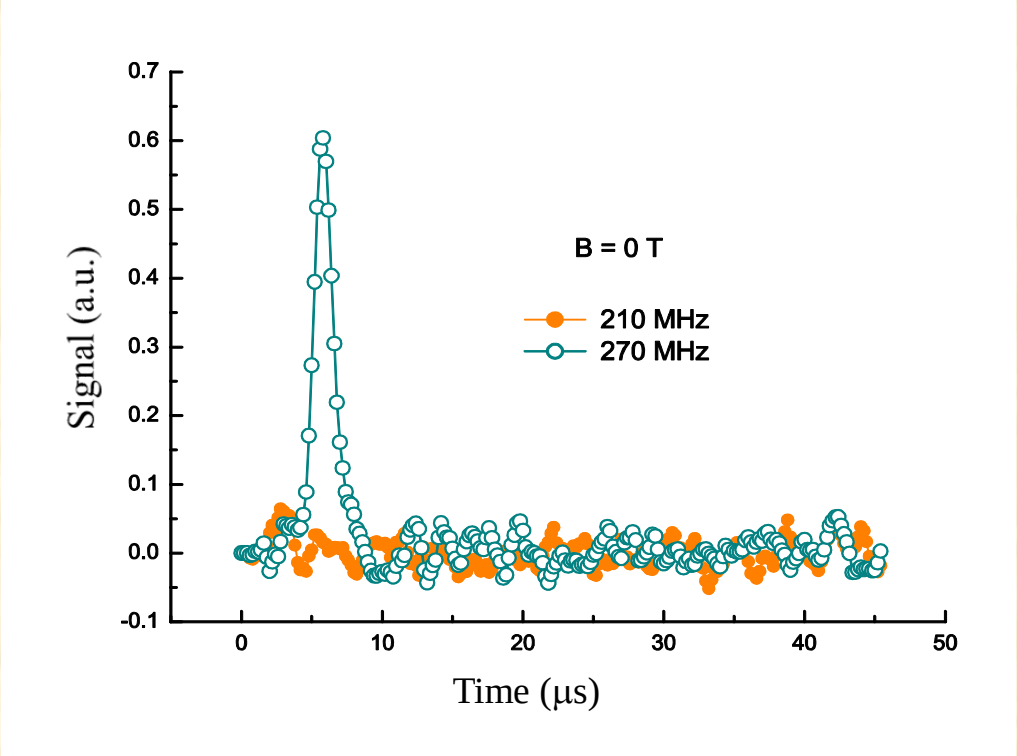
Grafite ferromagnético

Determinação experimental de B_{hf} por **RMN de ^{13}C** em campo zero:

$$f_{ZF\text{-}NMR} = \frac{\gamma(^{13}C)B_{hf}}{2\pi} \approx 200 - 230 \text{ MHz}$$

Experimental

Cálculos DFT



Freitas et al. "Hyperfine magnetic field in ferromagnetic graphite".
http://arxiv.org/abs/1406.1119

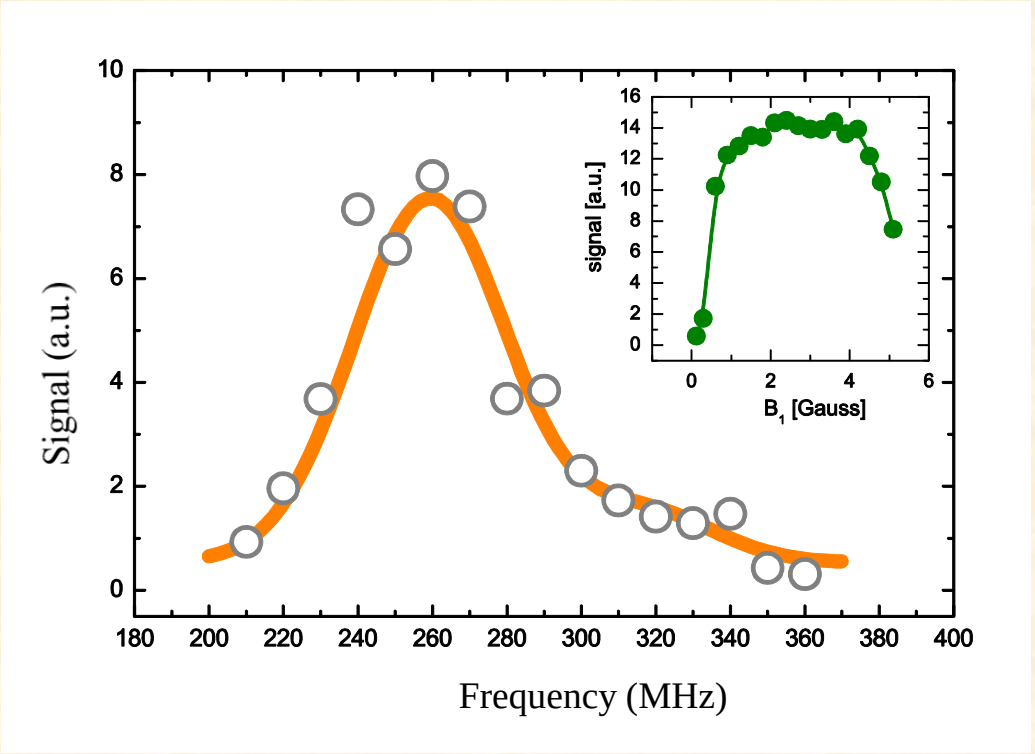
Grafite ferromagnético

Determinação experimental de B_{hf} por **RMN de ^{13}C** em campo zero:

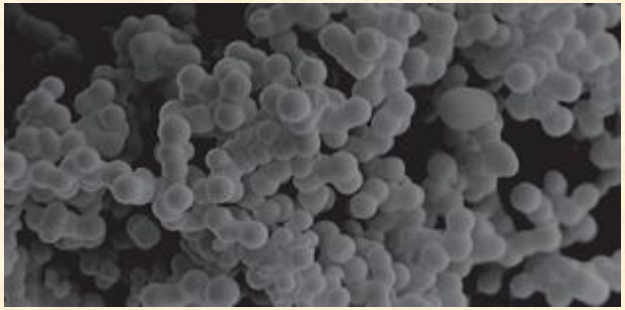
$$f_{ZF\text{-}NMR} = \frac{\gamma(^{13}C)B_{hf}}{2\pi} \approx 200 - 230 \text{ MHz}$$

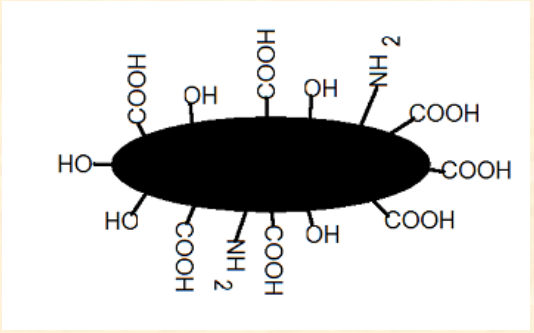
Experimental

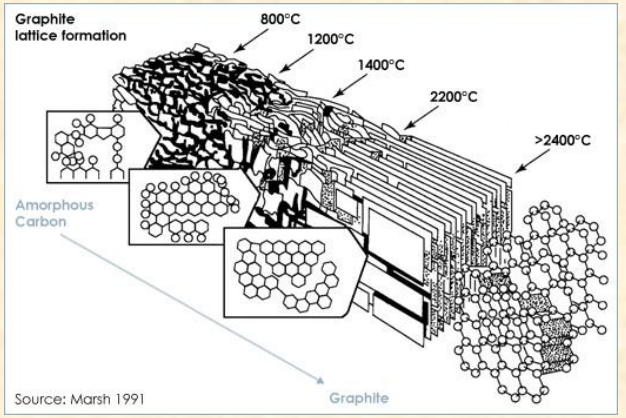
Cálculos DFT



Freitas et al. "Hyperfine magnetic field in ferromagnetic graphite".
http://arxiv.org/abs/1406.1119



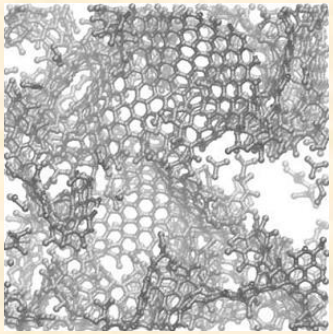


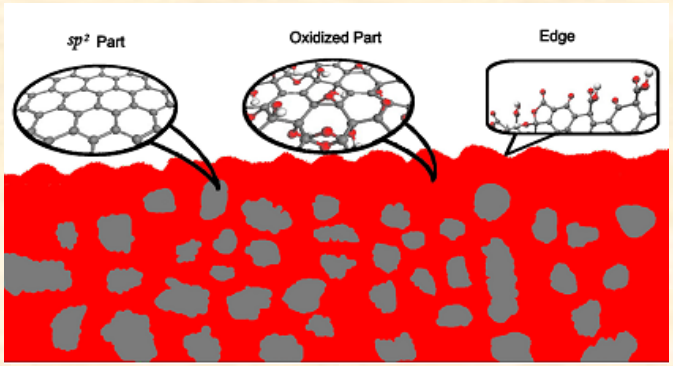


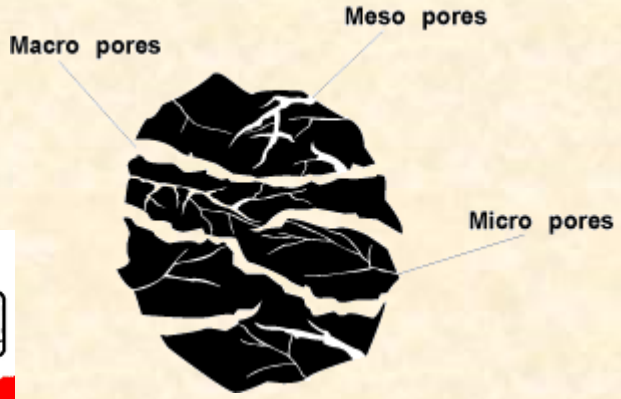
Métodos de RMN no estado sólido

^{1}H, ^{13}C, ^{15}N, ^{19}F,

^{31}P, ^{129}Xe, …

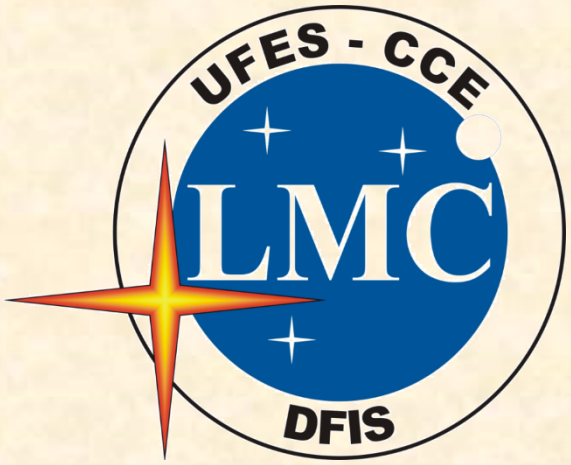






Agradecimentos

Grupos de pesquisa:

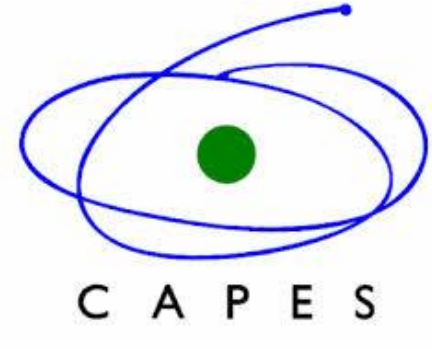


Agradecimentos

Colaborações:

Agradecimentos

Apoio / Financiamento:



Curva da Jurema, Vitória (ES)