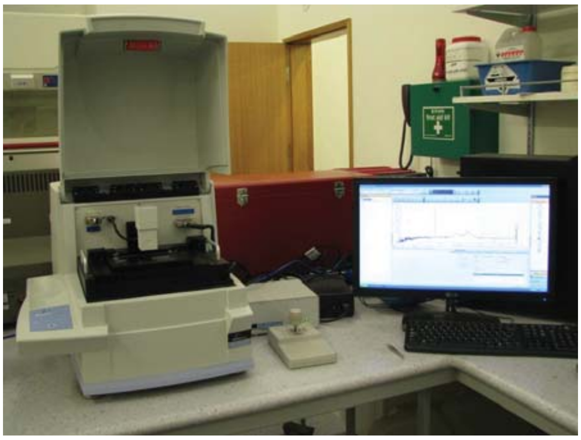
STUDYING CARBONISATION WITH RAMAN SPECTROSCOPY



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Chars and Carbonised Chars

- Mostly (sp^2) carbon in aromatic (and/or graphene-like) structures. Most of the major chemical changes and mass loss occur early (HTT < 400°C).
- Product properties change drastically when the heat treatment temperature (HTT) used in the production process is increased.

Nanostructural development of carbonaceous material (from hydrogen-rich amorphous carbon towards tangled network of graphene-like sheets).

Chars prepared at 300-400°C → **Well-carbonised Chars prepared at 700-1000°C**

≈ 6 orders of magnitude increase in electrical conductivity

≈ 1-2 orders of magnitude increase in specific surface area (N_2, BET)

≈ 1 order of magnitude increase in hardness and modulus

(Antal and Grønli 2003) (Rhim *et. al.* 2010) (Keiluweit *et. al.* 2010) (Zickler *et. al.* 2006) (Franklin 1951) (Jenkins & Kawamura 1976) (Rouzaud and Oberlin 1989) (McBeath and Smernik 2011)(McDonald-Wharry *et. al.* 2013)

Aims of Raman Analysis

- Develop a method for reliably measuring the extent of chemical/nanostructural changes which have occurred during the carbonisation of biomass. Be able to use this method to rapidly estimate the heat treatment temperatures (HTTs) employed in the production of a given char sample. (Quality control, product consistency after scale-up).

- Continue testing a hypothesis about carbonised charcoals being more chemically and nanostructurally similar to thermally-reduced graphene oxide(s) than to other proposed structural analogues such as fullerenes and graphite.

- Start correlating Raman measurements to other values and properties considered important (such H/C atom ratios from IBI Guidelines).

(International Biochar Initiative 2012) (McDonald-Wharry *et. al.* 2013)

Heating under an inert or oxygen-poor atmosphere

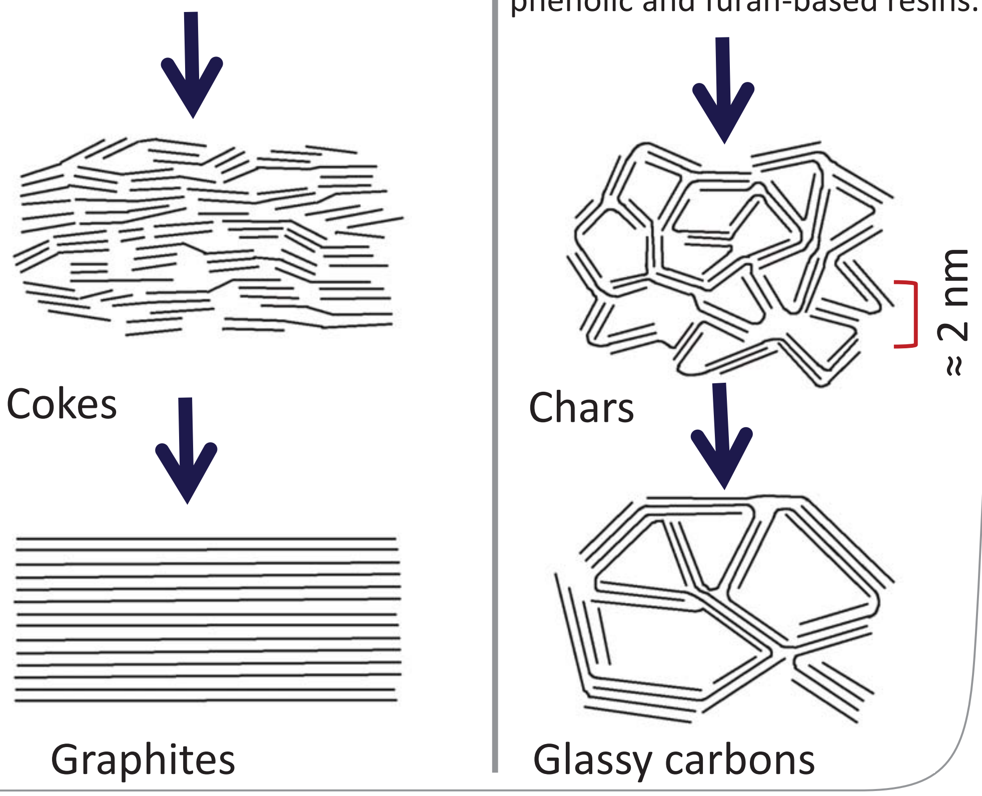
500°C to 1000°C

(Franklin. 1951)
(Jenkins & Kawamura. 1976)
(Oberlin. 1989)

1500°C to 3000°C

Precursors poor in oxygen
Pitch, coking coals, PAHs, heavy petroleum fractions.

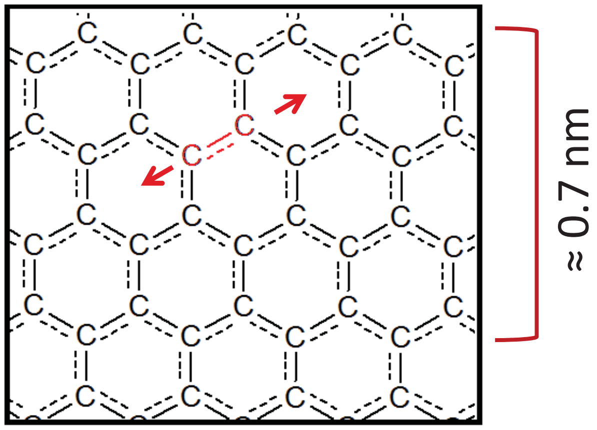
Precursors rich in oxygen
Carbohydrates, lignocellulosic biomass, low-rank coals, lignite, phenolic and furan-based resins.



Raman Spectroscopy of graphite and graphene-like materials

- Raman spectrometer excites an area of the sample with a laser (785 nm), then collects and records Raman scattering as a spectrum.
- Bands and signals on the Raman spectrum usually relate to the stretching of various bonds and lattice vibrations.

G band
Stretching of carbon-carbon sp^2 bonds



(Robertson 2002)(Ado *et. al.* 2010)(Gupta *et. al.* 2008)

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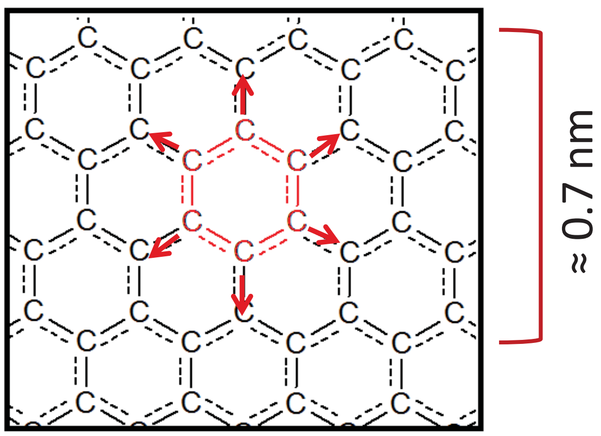
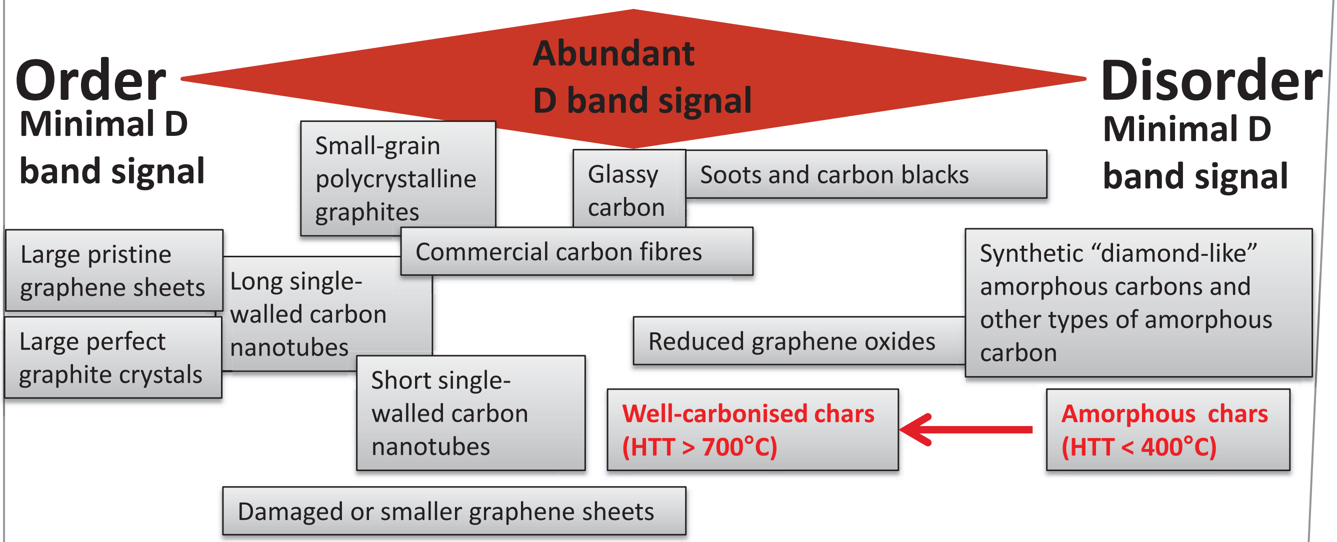
D band
Breathing mode of hexagonal rings

Only seen in Raman spectrum if ring is close (< 10 nm) to sheet edge or other defect



(Robertson 2002)(Ado *et. al.* 2010)(Gupta *et. al.* 2008)

Order, Disorder and the D band



- Maximum intensity of the D band relative to the G band occurs when nanostructure has ordered graphene-like domains where each hexagonal ring is within about 4 nanometres of an edge or other defect.

(Robertson 2002)(Ado *et. al.* 2010) (Gupta *et. al.* 2008)

Sample Production and Precursors

- Some precursors (harakeke leaf fibres, sucrose sugar crystals) were carbonised in electric furnaces under low oxygen conditions (N_2 purged or vacuum evacuated quartz vessels).

- Radiata pine wood derived chars produced in Massey's gas-fired drum pyrolyser. Other Radiata pine wood and pyrolysis tars were also carbonised in an electric furnace.

- Samples were heated to a range of HTTs between 300°C and 1000°C (usually 20 min dwell time at max temperature and HTTs were calculated from average thermocouple reading over 12 min where they were highest).

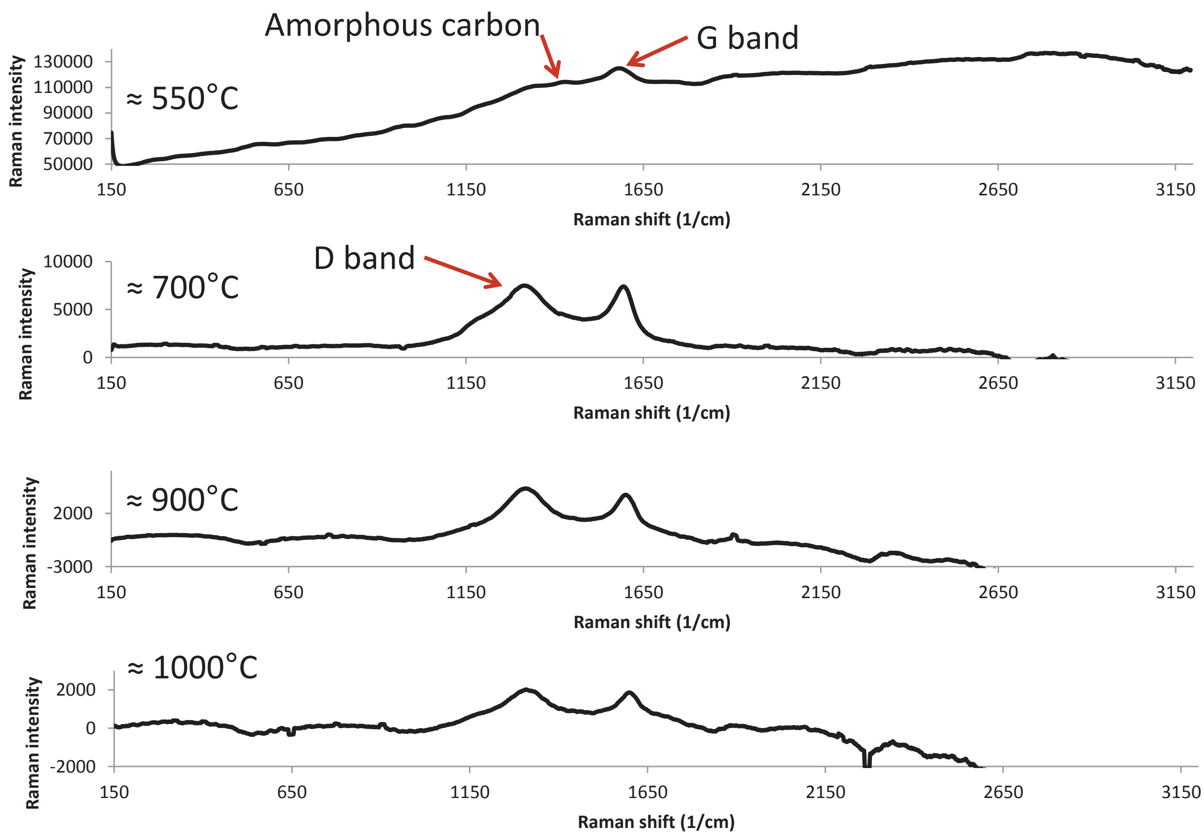
- Samples were analysed using the Raman spectrometer after they had cooled to room temperature.

Raman Methodology: Overview

- Developed method which will obtain adequate spectra from a wide range of different carbonaceous samples.
- Analysed a wide range of carbonaceous materials using the same excitation laser wavelength, the same data processing method, and similar instrument settings. (Goal of fair comparisons).
- Chars, carbonised chars, graphene oxides, and thermally-reduced graphene oxides all were analysed.
- Purchased, borrowed, and scavenged samples of various graphites, fullerenes, single-walled carbon nanotubes, glassy carbons, and PAN-derived carbon fibres for analysis and comparison.

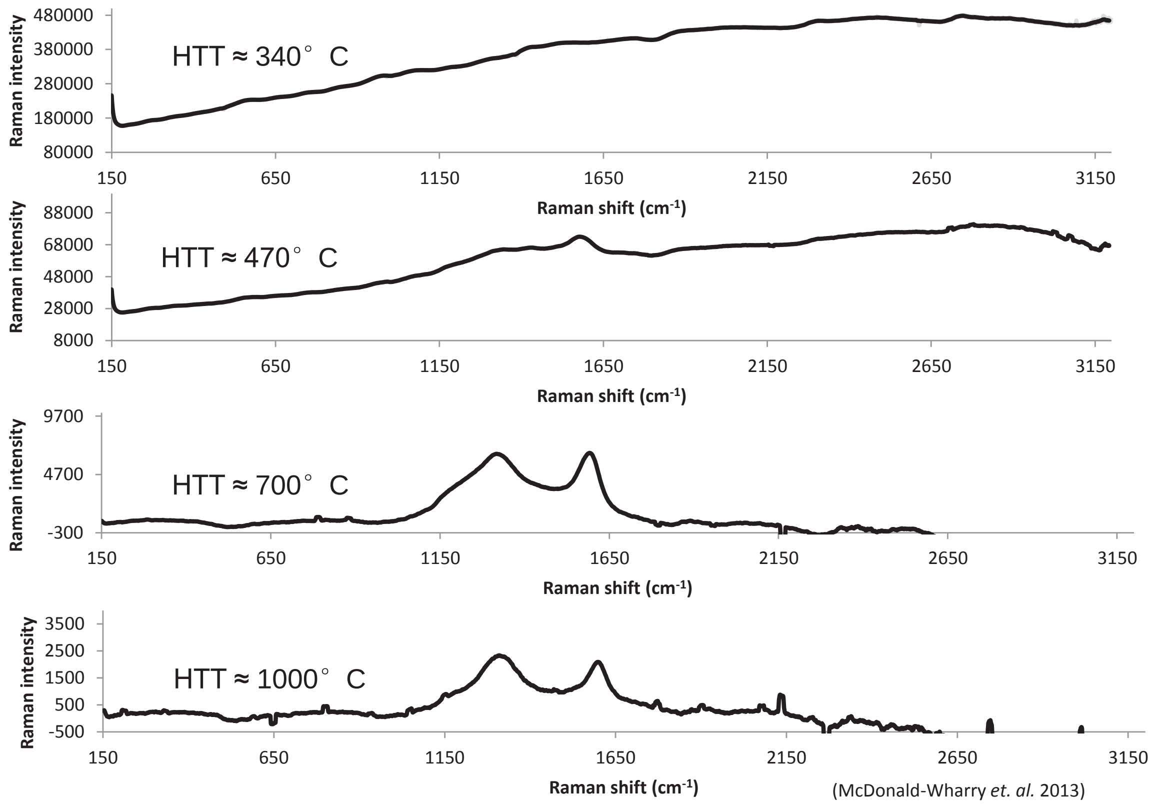
(McDonald-Wharry *et. al.* 2013)

Sucrose Chars and Carbonised Chars



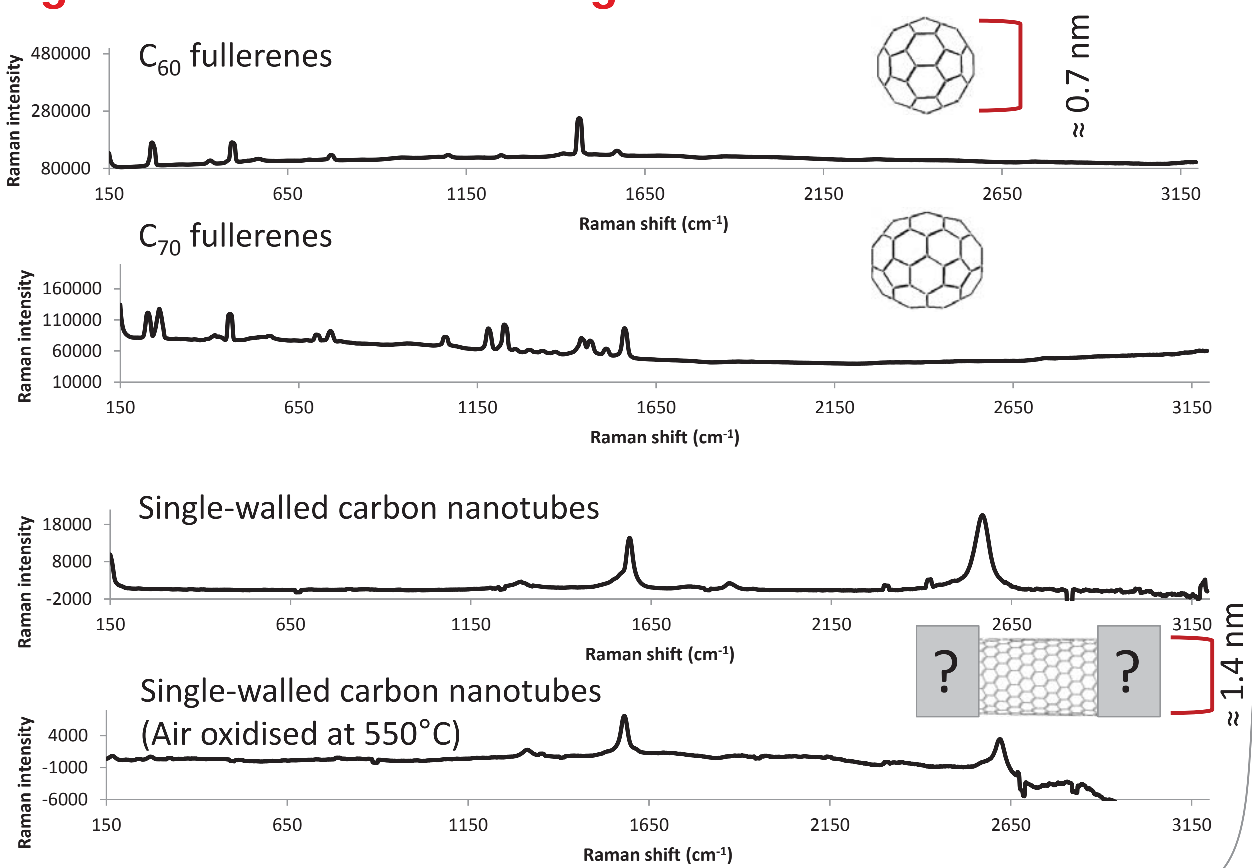
(McDonald-Wharry *et. al.* 2013)

Radiata Pine Chars and Carbonised Chars



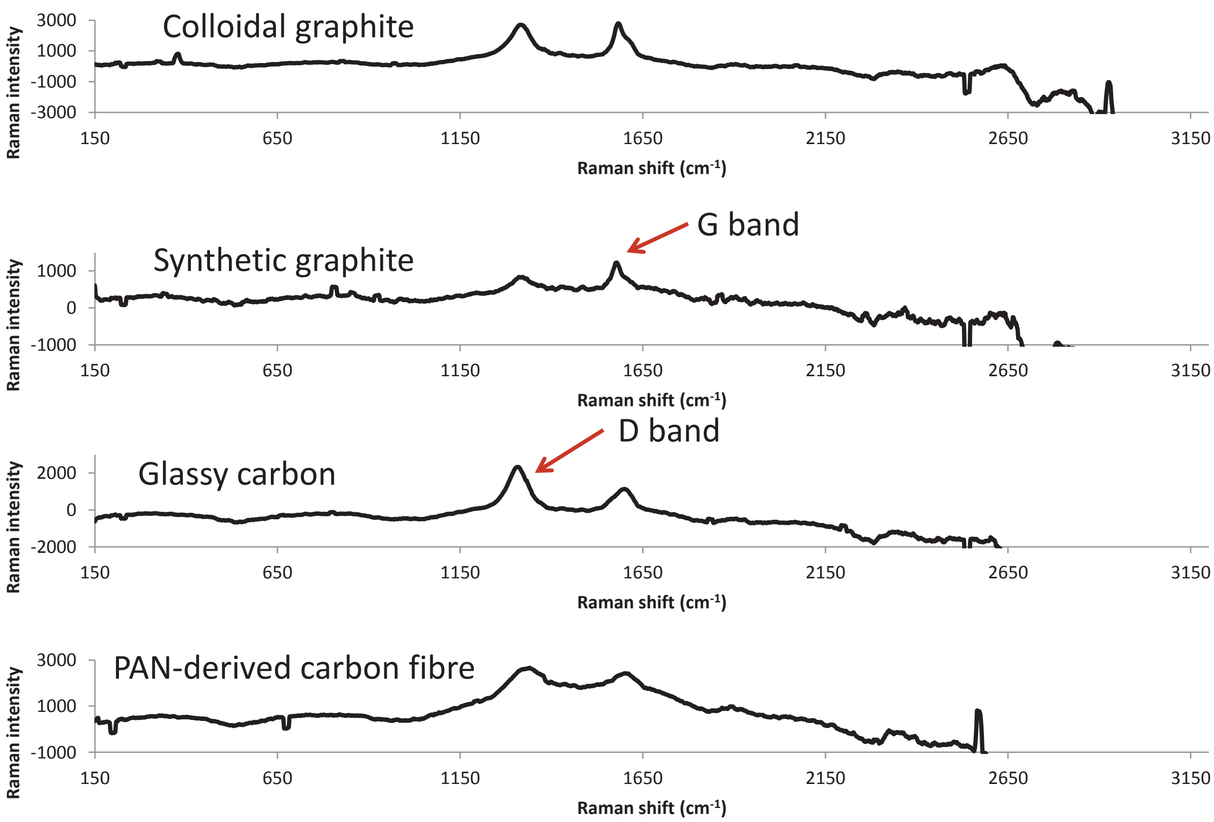
(McDonald-Wharry *et. al.* 2013)

Regular Fullerenes and Single-walled Carbon Nanotubes



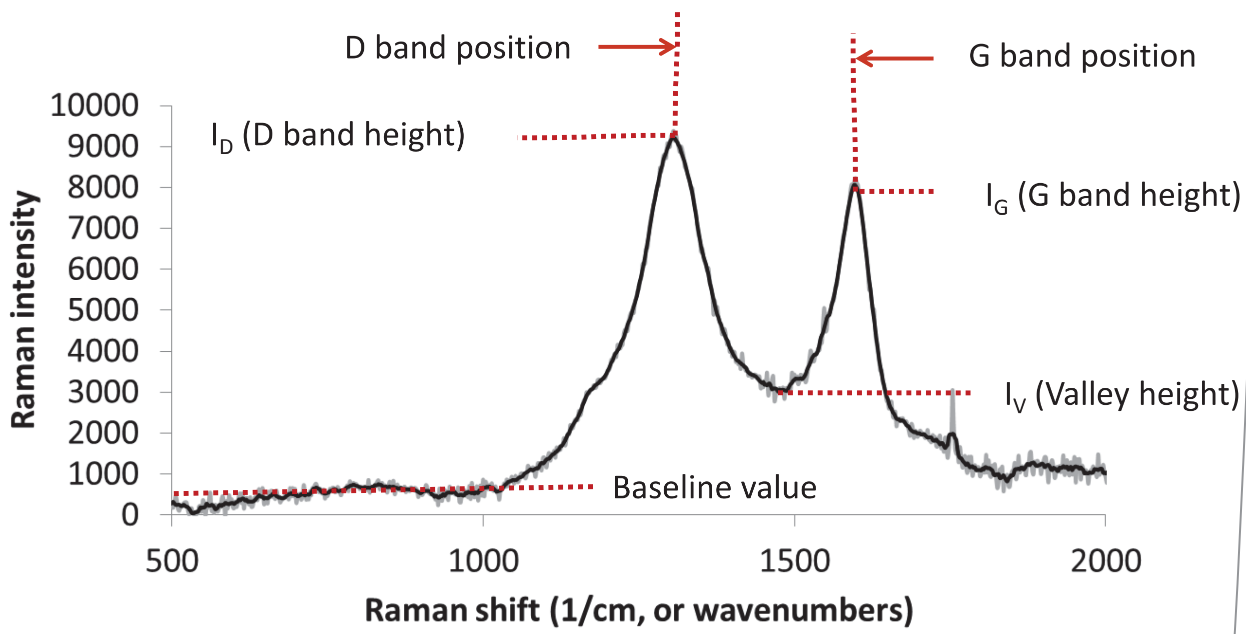
(McDonald-Wharry *et. al.* 2013)

Graphites, Glassy Carbon, & PAN-derived Carbon Fibre

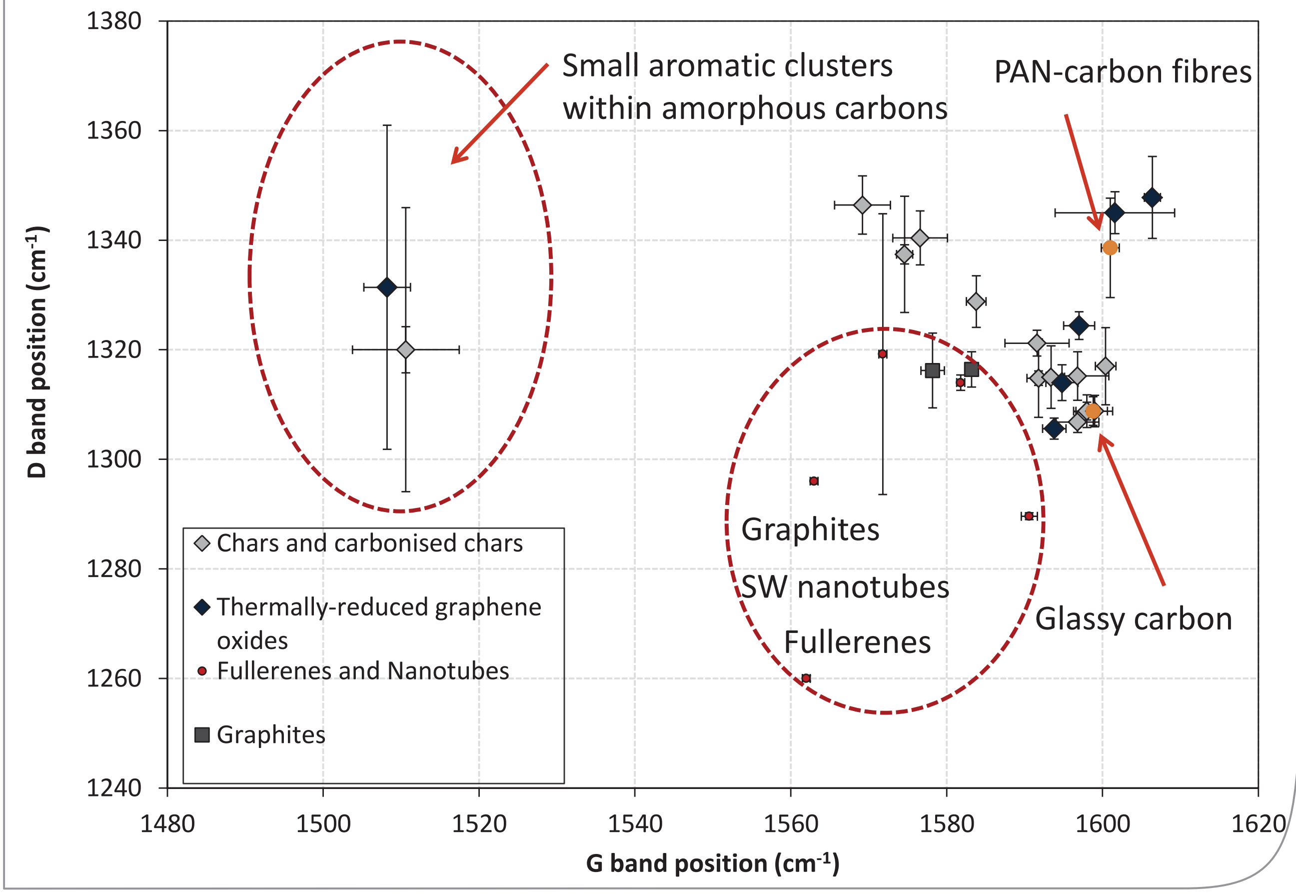


(McDonald-Wharry *et. al.* 2013)

Data Processing and Spectral Parameters



Map of D band and G band positions



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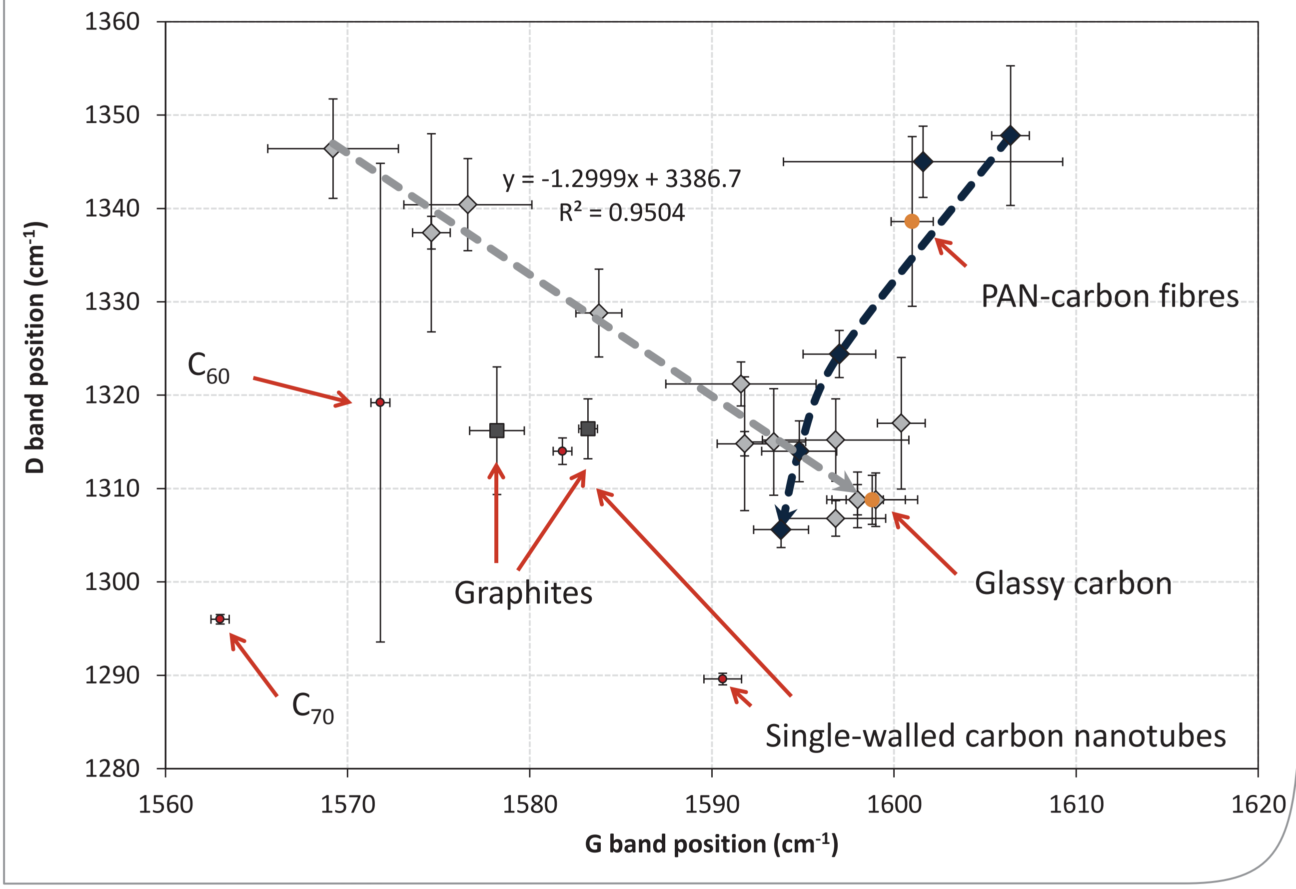
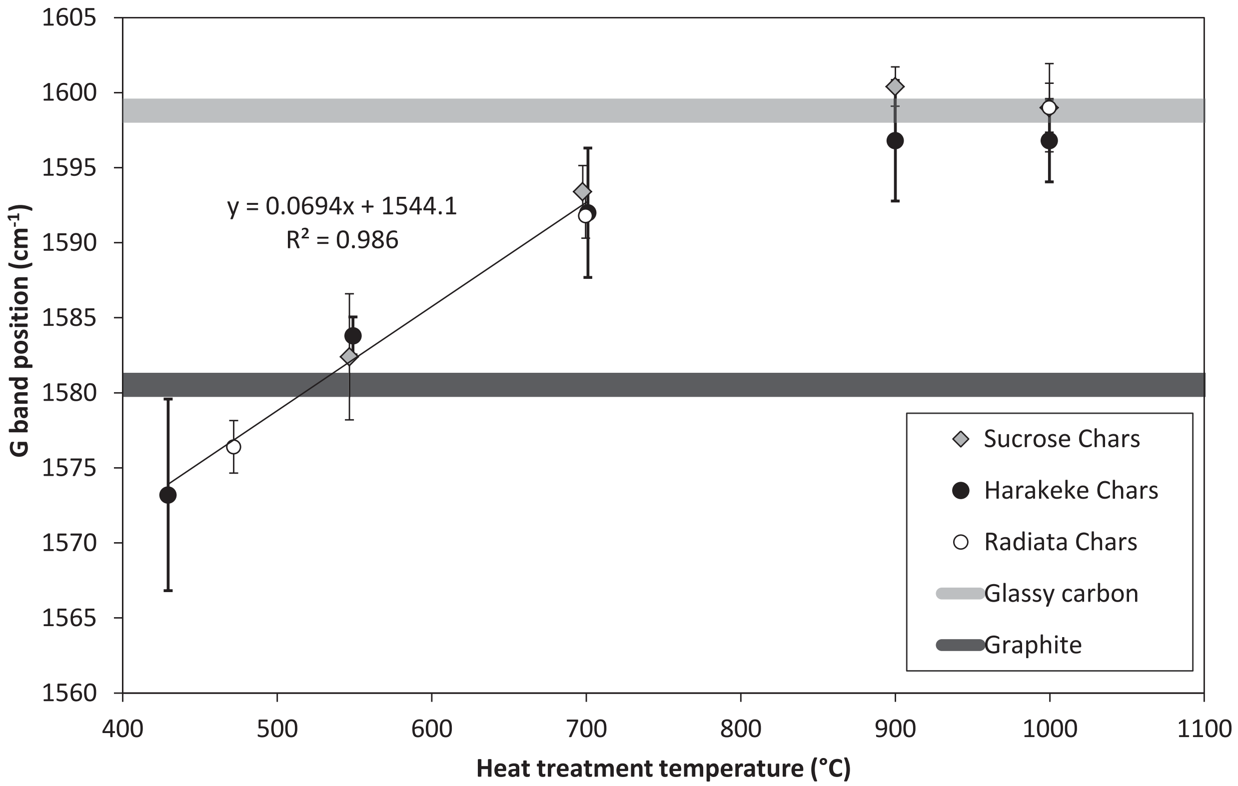
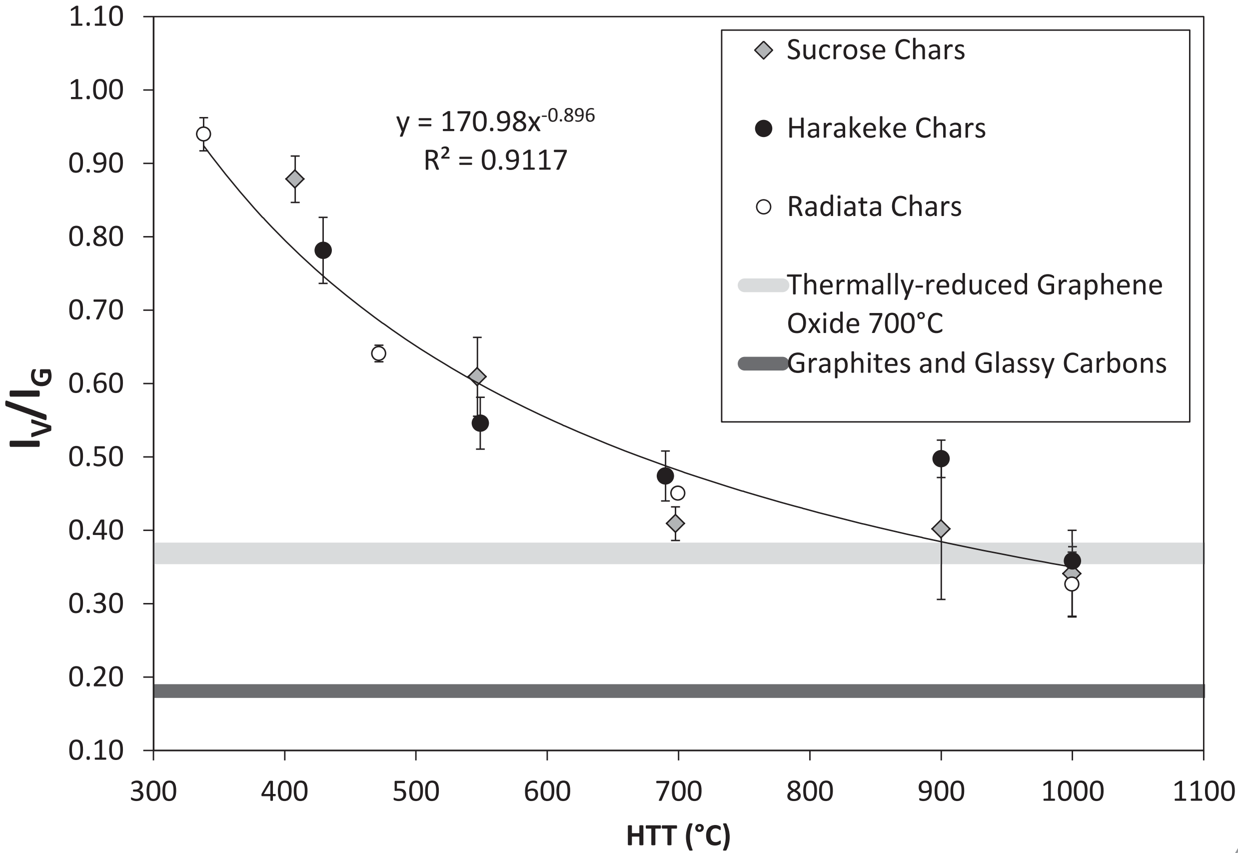


G band positions and heat treatment temperatures



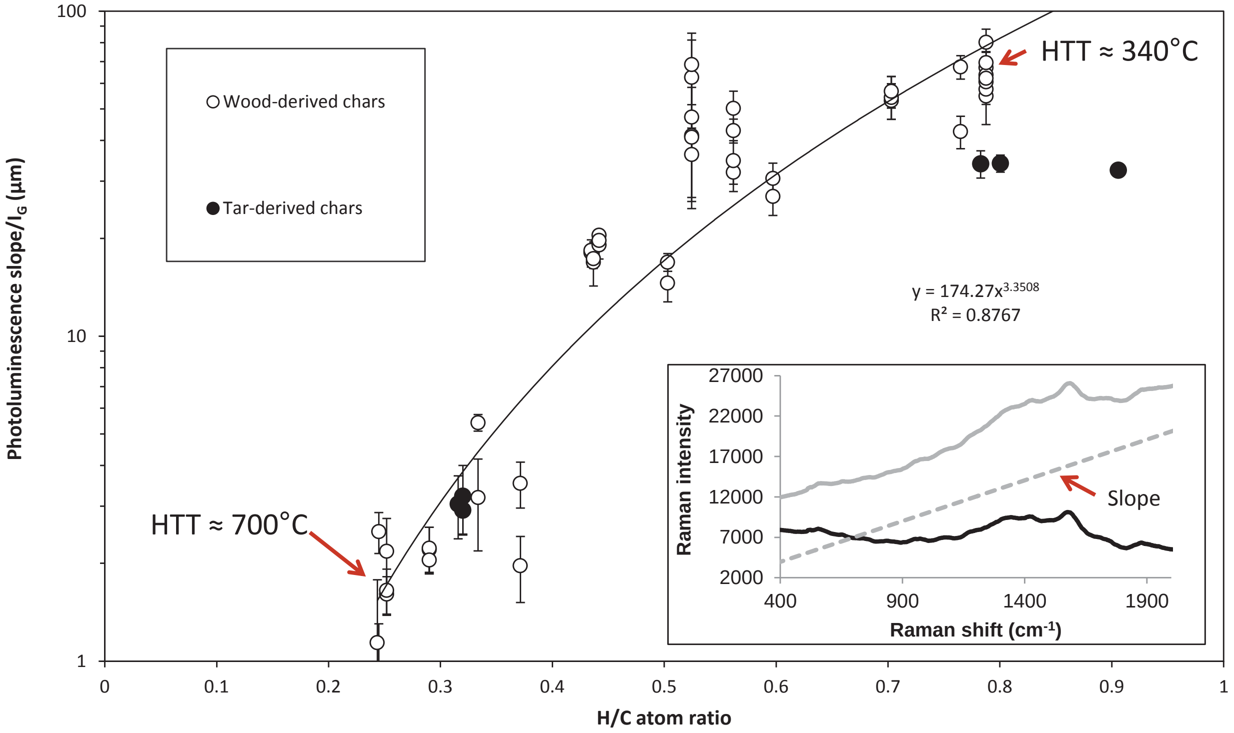
(McDonald-Wharry *et. al.* 2013)

(Valley height) / (G band height) ratio and heat treatment temperatures



(McDonald-Wharry *et. al.* 2013)

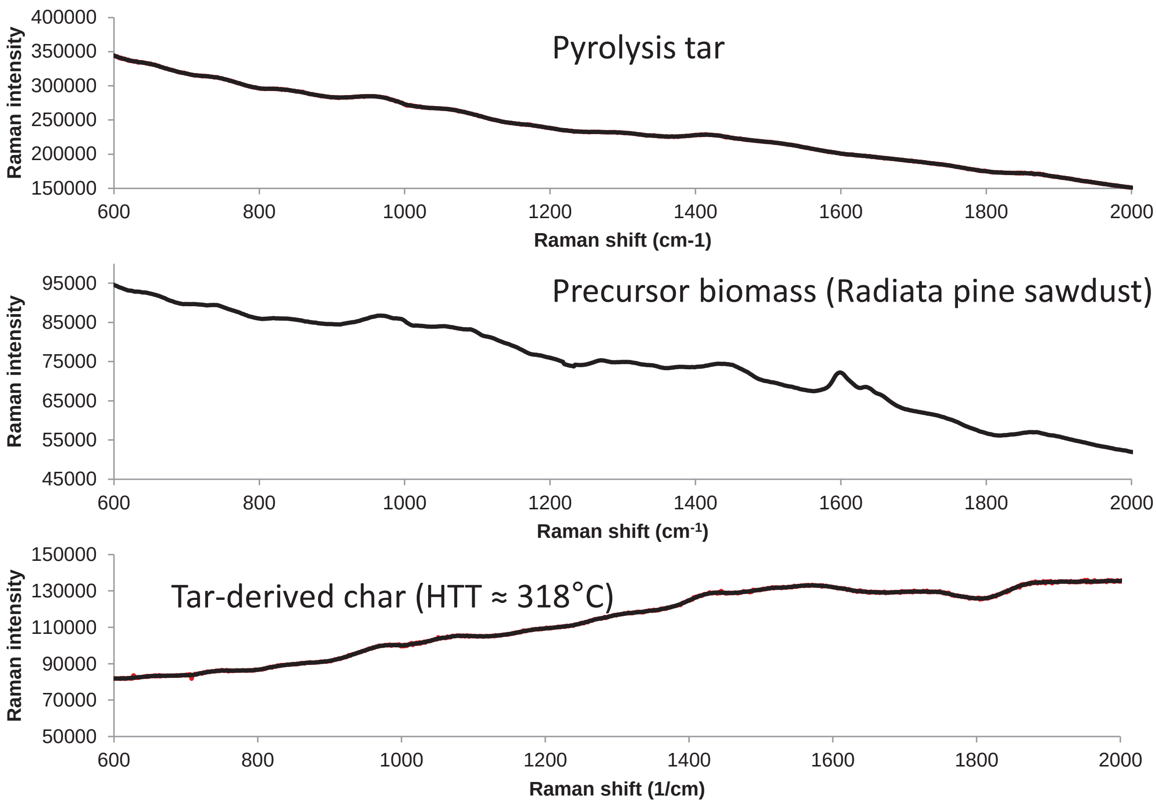
(Photoluminescence slope) / (G band height) ratio and H/C ratios



Similar trend and scatter to synthetic hydrogenated amorphous carbon films

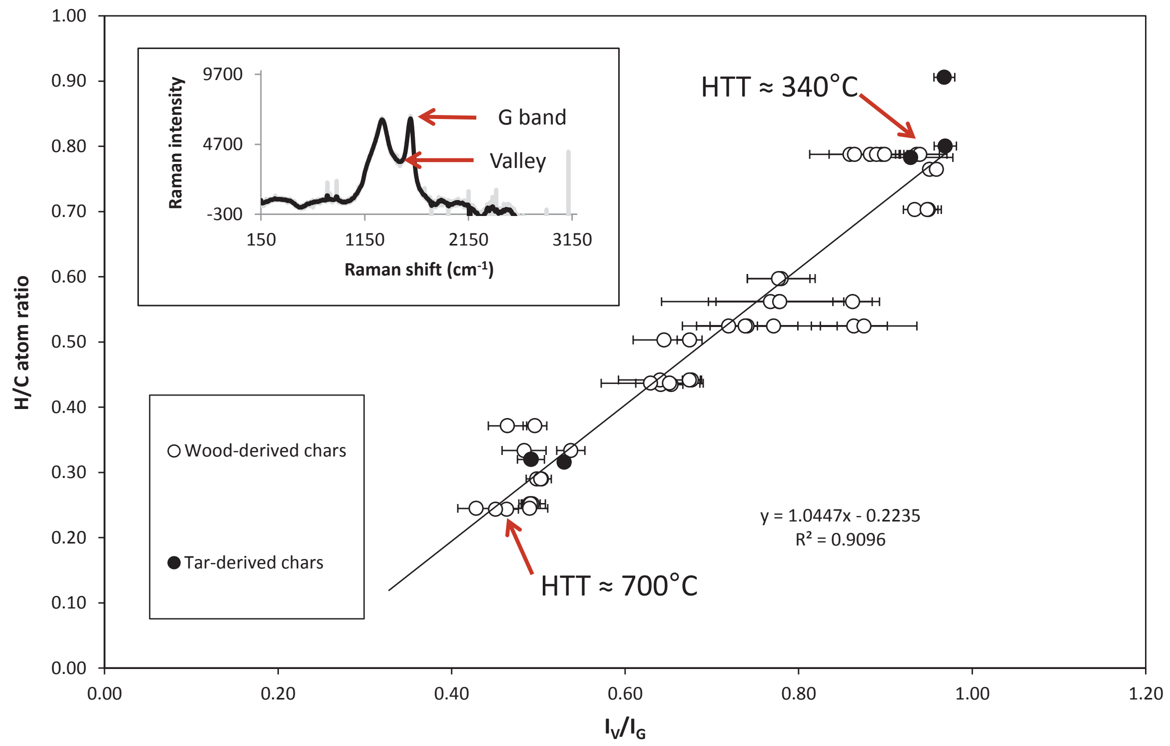
(Casiraghi *et. al.* 2005)

Photoluminescence slopes and/or fluorescence slopes



Amorphous chars generate positive slopes, but tars and unpyrolysed biomass generate negative slopes in Raman spectra (when using 785 nm excitation)

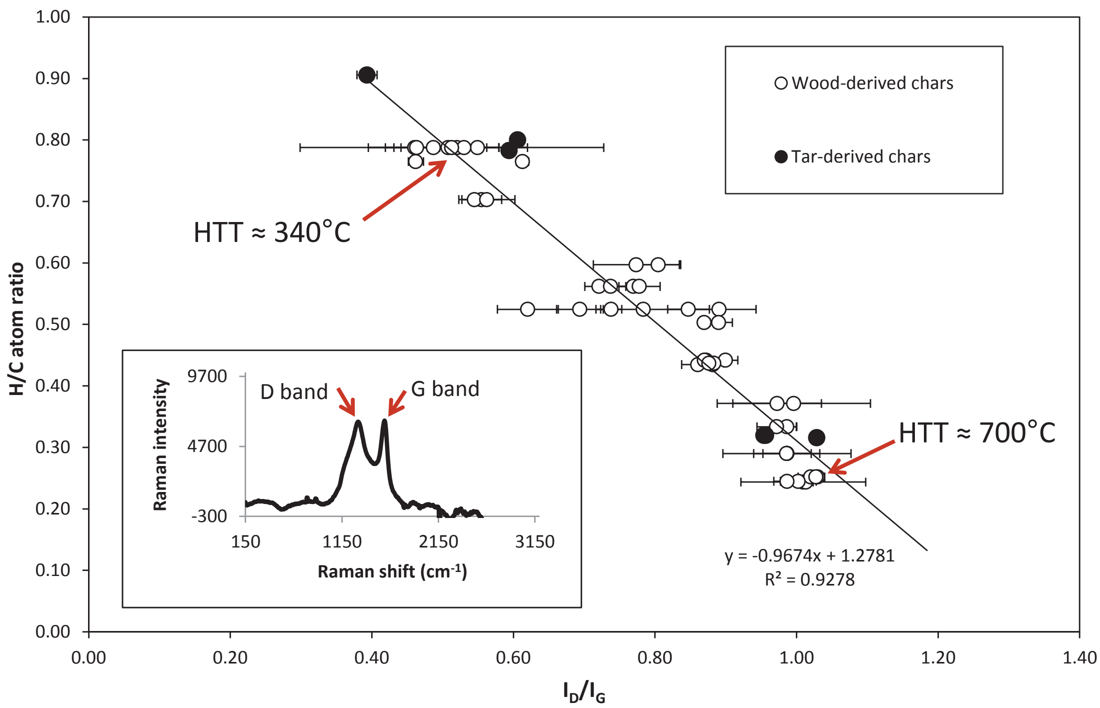
(Valley height) / (G band height) ratio and H/C ratios



Raman I_V/I_G ratios correlates to the H/C ratios obtained from elemental analysis of these Radiata pine derived chars.

Interpretation: Removal of hydrogen-rich amorphous carbon with increasing HTT

(D band height) / (G band height) ratio and H/C ratios



Raman I_D/I_G ratios also correlates to the H/C ratios obtained from elemental analysis of these Radiata pine derived chars.

Interpretation: Growth of hydrogen-poor graphene-like structures with increasing HTT)

Conclusions

- A number of Raman parameters can be used to monitor the extent of carbonisation in chars. G band position correlates well and is measurable over the widest range of precursors and temperatures.
- I_V/I_G and I_D/I_G height ratios also useful for evaluating lower HTT chars and the conversion of amorphous carbon into polyaromatic/graphene-like carbon. So far I_V/I_G (and I_D/I_G) values correlate well with H/C atom ratios for Radiata pine derived chars, indicating that Raman analysis could be used to estimate H/C_{org} values.
- Carbon nanostructure appears to become independent of precursor as HTT increases towards 700-1000°C
- Positive slopes which occur in Raman spectra of low HTT chars are different to the negative slopes which occur in Raman spectra obtained from pyrolysis tars and biomass precursors.

Acknowledgements

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References

Ado, J., G. Dresselhaus and M. S. Dresselhaus (2010). Raman spectroscopy in nanoscience and nanometrology: carbon nanotubes, nanographite and graphene. Hoboken, NJ, USA, Wiley-VCH.
Antal, M. J. and M. Gronli (2003). "The art, science, and technology of charcoal production." Industrial & Engineering Chemistry Research 42(8): 1619-1640.
Casiraghi, C., F. Piazza, A. C. Ferrari, D. Grambole and J. Robertson (2005). "Bonding in hydrogenated diamond-like carbon by Raman spectroscopy." Diamond and Related Materials 14(3–7): 1098-1102.
Franklin, R. E. (1951). "Crystallite growth in graphitizing and non-graphitizing carbons." Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences 209(1097): 196-218.
Gupta, A. K., T. J. Russin, H. R. Gutiérrez and P. C. Eklund (2008). "Probing Graphene Edges via Raman Scattering." ACS Nano 3(1): 45-52.
International Biochar Initiative (2012)
Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil IBI May 2012
Jenkins, G. M. and K. Kawamura (1976). Polymeric Carbons - carbon fibre, glass and char. Cambridge, Cambridge University Press.
Keiluweit, M., P. S. Nico, M. G. Johnson and M. Kleber (2010). "Dynamic molecular structure of plant biomass-derived black carbon (biochar)." Environmental Science & Technology 44(4): 1247-1253.
McBeath, A. V., R. J. Smernik, M. P. W. Schneider, M. W. I. Schmidt and E. L. Plant (2011). "Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of wood charcoal using NMR." Organic Geochemistry 42(10): 1194-1202.
McDonald-Wharry, J., M. Manley-Harris and K. Pickering (2013). "Carbonisation of biomass-derived chars and the thermal reduction of a graphene oxide sample studied using Raman spectroscopy." Carbon 59(0): 383-405.
Rhim, Y. R., D. J. Zhang, D. H. Fairbrother, K. A. Wepasnick, K. J. Livi, R. J. Bodnar and D. C. Nagle (2010). "Changes in electrical and microstructural properties of microcrystalline cellulose as function of carbonization temperature." Carbon 48(4): 1012-1024.
Robertson, J. (2002). "Diamond-like amorphous carbon." Materials Science and Engineering: R: Reports 37(4–6): 129-281.
Rouzaud, J. N. and A. Oberlin (1989). "Structure, microtexture, and optical-properties of anthracene and saccharose-based carbons." Carbon 27(4): 517-529.
Zickler, G. A., T. Schoberl and O. Paris (2006). "Mechanical properties of pyrolysed wood: a nanoindentation study." Philosophical Magazine 86(10): 1373-1386.

Questions?