
Rosalind Franklin's work on coal, carbon, and graphite

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Rosalind Franklin's earliest research involved studies of coal, carbon, and graphite. She made a number of enduring contributions in these areas, most notably identifying the fundamental distinction between graphitising and non-graphitising carbons. Her work on carbon also provided a valuable background for her later biological work.

Rosalind Franklin's role in unravelling the structure of DNA is very widely known, mainly as a result of James Watson's book 'The double helix' (1968) and the BBC film 'Life story' (1987). What is less well known is that she made fundamental and enduring contributions to several other areas of science both before and after the relatively short time she spent working on DNA at King's College London. After leaving King's in early 1953, she moved to Birkbeck College, London, where she carried out important work on viruses and RNA. Her earliest research had been carried out during the war on coal and she then spent four years in Paris studying the structure of carbons using X-ray diffraction. She continued to write papers on carbon and graphite until her early death in 1958, and many of these papers have become classics. The table gives what is believed to be a complete listing of her papers on coal, carbon, and graphite, with the most important ones highlighted. The main aim of this article is to summarise the most important aspects of Franklin's work on carbon, and to demonstrate the continuing relevance of many of her discoveries. A brief assessment is also made of the way in which her studies of carbon prepared her for the subsequent work on DNA. First, a few biographical details should be given.

Rosalind Elsie Franklin was born into a prosperous London banking family on 25 July 1920. She attended St Paul's Girls' School in London and went on to study chemistry at Newnham College, Cambridge, graduating in 1941. After graduation she initially began a research project on the polymerisation of acetaldehyde and formic acid under the supervision of Ronald Norrish, Professor of Physical Chemistry at Cambridge. However, this did not progress well, and her relationship with Norrish seems to have been a strained one.¹ Therefore, when the opportunity arose to take up a post with the British Coal Utilisation Research Association at Kingston upon Thames, Franklin was happy to accept. Another reason for the move may have been her desire to carry out work which would be of more direct value

Rosalind Franklin's published work on coal, carbon, and graphite: the most important papers, in terms of the number of citations received, are marked with an asterisk

University of Cambridge

'The physical chemistry of solid organic colloids with special relation to coal and related materials', PhD thesis, 1945

CURA

'Thermal expansion of coals and carbonized coals', *Transactions of the Faraday Society*, 1946, **42B**, 289–294 (with D. H. Bangham)

'A note on the true density, chemical composition, and structure of coals and carbonized coals', *Fuel*, 1948, **27**, 46–49

*'A study of the fine structure of carbonaceous solids by measurements of true and apparent densities. Part I. Coals', *Transactions of the Faraday Society*, 1949, **45**, 274–286

*'A study of the fine structure of carbonaceous solids by measurements of true and apparent densities. Part II. Carbonized coals', *Transactions of the Faraday Society*, 1949, **45**, 668–682

'A structural model for coal substance', *Fuel*, 1949, **28**, 231–238 (with D. H. Bangham, W. Hirst, and F. A. P. Maggs)

Paris

'Influence of bonding electrons on the scattering of X-rays by carbon', *Nature*, 1950, **165**, 71–72

*'The interpretation of diffuse X-ray diagrams of carbon', *Acta Crystallographica*, 1950, **3**, 107–121

'The structure of carbon', *Journal de Chimie Physique*, 1950, **47**, 573–575

'Graphitizable and nongraphitizable carbons', *Comptes Rendus*, 1951, **232**, 232–234

*'The structure of graphitic carbons', *Acta Crystallographica*, 1951, **4**, 253–261

*'Crystallite growth in graphitizing and non-graphitizing carbons', *Proceedings of the Royal Society of London A*, 1951, **209**, 196–218

Birkbeck

'Graphitizing and non-graphitizing carbon compounds. Formation, structure and characteristics', *Brennstoff-Chemie*, 1953, **34**, 359–361

'Homogeneous and heterogeneous graphitization of carbon', *Nature*, 1956, **177**, 239

'The alpha dimension in graphite', *Acta Crystallographica*, 1951, **4**, 561–562 (with G. E. Bacon)

'Changes in the structure of carbon during oxidation', *Nature*, 1957, **180**, 1190–1191 (with J. D. Watt)



1 Rosalind Franklin in about 1949 (National Portrait Gallery)

to the war effort: coal's importance to Britain's wartime economy can hardly be overestimated. Franklin's work focused on the porosity of coal, and she made a number of fundamental contributions in this area. After the war, she was keen to move on from coal research and began to seek a post abroad. She wrote to her friend Adrienne Weill in Paris, who put her in touch with the leading French chemist Marcel Mathieu. Through Mathieu she obtained in 1946 a position at the Laboratoire Central des Services Chimiques de l'Etat in Paris, working under Jacques Méring. It was here that she carried out her most important work on carbon, which involved X-ray diffraction studies of the graphitisation process. The photograph shown in Fig. 1 was taken during her time in France, which by all accounts was a very happy one.

By 1950, Franklin was ready to move back to England. She wrote to John T. Randall, head of the Biophysical Laboratory at King's College London, who offered her a post for three years supported by a Turner–Newall fellowship. Initially the intention was that she would work on X-ray diffraction of proteins in solution, an area of research in which her experience with coals would have been useful. In November 1950, however, Randall wrote to her suggesting that she instead should work on DNA fibres. This field had been pioneered by Maurice Wilkins at King's, and Randall's letter did not make it clear whether Wilkins or Franklin was to be in charge of the DNA work. This produced much misunderstanding between the two, and made Franklin's time at King's an unhappy one. Ultimately it was Franklin's superb X-ray pictures which enabled Watson and Crick to solve the structure. From 1953 to 1958 Franklin worked in the Crystallography Laboratory at Birkbeck. While there she continued to write papers on carbon and on DNA and began a project on the molecular structure of the tobacco mosaic virus (TMV). She collaborated on studies showing that the RNA in that virus was embedded in its protein rather than in the central cavity and that TMV RNA was a single strand helix, rather than the

double helix found in the DNA of bacterial viruses and higher organisms. Rosalind Franklin died of cancer on 16 April 1958 at the age of 37. A number of biographical sources are available,^{1–4} and a new biography is currently being prepared by Brenda Maddox.

Coal

The enormous economic importance of coal, and the scientific challenges involved in understanding its evolution and composition and in optimising its utilisation, have attracted many brilliant scientists to the field. In the twentieth century these included such diverse characters as Marie Stopes (1880–1958), better known as author of 'Married love' than for her scientific work, and Jacob Bronowski (1908–74), mathematician, writer, and presenter of the BBC television series 'The ascent of man'. Marie Stopes was appointed lecturer in botany at the University of Manchester in 1904, where she was the first woman to lecture in science. She was interested in coal as a fossilised plant material and developed a classification system for coals based on their morphology which is still in use today. In this system the carbon containing constituents of coal, known as 'macerals' (by analogy with the minerals which make up inorganic rock), are grouped into types such as vitrinites and fusinites depending on the structure of the fossilised plant tissue revealed by optical microscopy. Each type of maceral can be further classified in terms of its 'rank', a measure of the degree of coalification, which in turn determines the amount of heat it produces. The ranks, in increasing order, are lignite (or brown coal), subbituminous coal, bituminous coal, and anthracite.

In the early part of the century, optical microscopy and classical chemical analysis were the main methods used in coal research. In the 1930s and 1940s, however, a wide range of new techniques for the physical characterisation of solids became available, and it was partly a desire to exploit these new methods which led to the setting up in 1938 of the British Coal Utilisation Research Association (CURA), with laboratories at Leatherhead in Surrey. Following nationalisation of the coal industry in 1946, a further research establishment was set up near Cheltenham, with Bronowski as its first director. Much outstanding work was carried out in these new laboratories, often in collaboration with universities, giving the UK a strong position in coal science and technology.

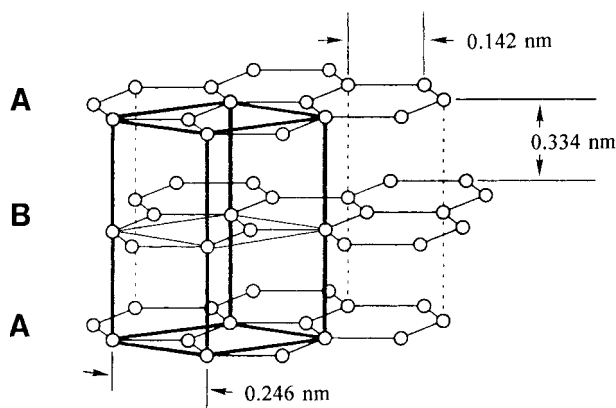
Rosalind Franklin's introduction to the study of coal came in 1942 when she joined the staff of CURA at Kingston upon Thames (the Leatherhead laboratory having been bombed). The director of CURA, Dr D. H. Bangham, allocated Franklin to a programme aimed at understanding the structure of coal through detailed studies of its density and porosity.

All coals are porous to a greater or lesser extent. Many of their properties, such as their reactivity and their capacity to adsorb gases and vapours, depend on this porosity. Some of the pores are macroscopic,

but most are on a much finer, molecular, scale, and it was these micropores which were of interest to Rosalind Franklin. Her chief method of investigating the porosity of coals was through measurements of density. A porous solid such as coal is associated with two different densities, the density of its purely solid structure, or true density, and the density of the whole material, including pores, or 'lump' density. The lump density is relatively easy to determine using the Archimedes liquid displacement method, always ensuring that one employs a liquid which does not penetrate fine pores, such as mercury. Measuring the true density of a porous material presents much more of a challenge. What is required is a gas or liquid which will penetrate all the pores of the solid, but will not combine with it chemically. In the case of coal, helium is believed to be the best displacement medium. In Franklin's work the true densities of a range of coals, from lignite to anthracite, were determined using helium, and the resulting values compared with the apparent densities obtained using water, methanol, hexane, and benzene.⁵ The results were rather surprising, and revealing. In the case of methanol, the measured densities were almost all *higher* than those measured using helium, even though the helium density should represent the true density of the solid. The explanation is that the methanol reacts chemically with the coal, resulting in a high uptake of the liquid, and a high apparent density. With hexane and benzene no chemical reaction occurred, but the measured densities also varied considerably from those determined using helium, in most cases being lower. Indeed, some of the density values obtained using these liquids differed very little from the lump densities. This was taken to imply that the entrances to the pores contained constrictions, so that helium molecules could enter but the larger hexane and benzene molecules could not. In other words, the coal was behaving as a 'molecular sieve', allowing small molecules to pass through but excluding larger ones. This was probably the first demonstration of molecular sieve behaviour in any carbon. Today, carbon molecular sieves are of great value in industry where, among other things, they are used to separate nitrogen from oxygen in air.⁶

In addition to demonstrating molecular sieve behaviour in coals, Franklin also attempted to use her measurements to determine the fundamental nature of the carbon in these coals. She calculated that the density of a coal of zero hydrogen content would be 1.85 cm^3 . This led her to suggest that the carbon in coal cannot be graphitic in nature, since the density of pure graphite is 2.26 g cm^{-3} . Partly as a result of this conclusion, Bangham, Franklin, and two colleagues put forward a model for coal based on micelles, or colloidal clusters.⁷ However, we now know that Franklin's calculation of the density of carbon in coal was incorrect, and the micelle model is no longer given any credence.

Following her study of the true and apparent densities of untreated coals, Franklin carried out a



2 The structure of graphite, showing the unit cell

similar study on coals which had been carbonised at temperatures up to 1600°C .⁸ The carbonisation of coal is of course an important industrial process, resulting in the formation of either coke or of coalite type smokeless fuel, depending on the type of coal used. Carbonisation is usually accompanied by a loss in reactivity, and Franklin's work was aimed at understanding this. Through careful experimentation she was able to show that the loss in reactivity did not result from a reduction in the porosity of the coals; indeed, the fine structure porosity was found to *increase* on heat treatment. Instead, a decrease in the 'accessibility' of the pores was responsible for the fall in reactivity. In some cases the pores became completely sealed, so that even helium molecules were excluded. Closed porosity of this kind had not been observed in the fresh coals.

Coal is a complex and recalcitrant material, many features of which remain imperfectly understood even today. In her studies of the density and porosity of coal, Rosalind Franklin was able to achieve a number of insights into its microstructure which have stood the test of time. Some aspects of her work on coal, such as the density determinations, also proved valuable in her work on DNA.

X-ray diffraction of carbons and graphite

Solid carbons were among the first materials to be studied by X-ray diffraction (XRD). As early as 1917, Peter Debye and Paul Scherrer published a study of disordered carbons which showed that most of the atoms were present in hexagonal benzenelike rings.⁹ In 1924, J. D. Bernal showed that graphite has the well known layered structure shown in Fig. 2,¹⁰ while the structure of diamond had been solved by the Braggs in 1913.¹¹ The detailed structure of non-crystalline carbon materials, such as soot, coke, and char, however, presented more of a challenge. While Debye and Scherrer had established that these carbons contained hexagonal carbon rings, the way these were linked together remained unknown. Some workers suggested that char might have a three-dimensional network structure lying somewhere

between those of graphite and diamond, but there was no direct evidence for this. The distinction between char and coke was also not understood. The field remained in some disarray until Rosalind Franklin's work in the late 1940s and early 50s.

First papers

In a paper published in *Acta Crystallographica* in 1950, Franklin described XRD studies of a char prepared from the polymer polyvinylidene chloride.¹² By rigorous quantitative analysis of the diffraction data, she was able to propose the first reliable model for the structure of a char. In this model, 65% of the carbon is contained in individual graphite layers, rather perfect in structure but only about 1.6 nm in diameter, with the remainder of the carbon being disordered. Earlier models, based on three-dimensional network structures, were shown to be incorrect.

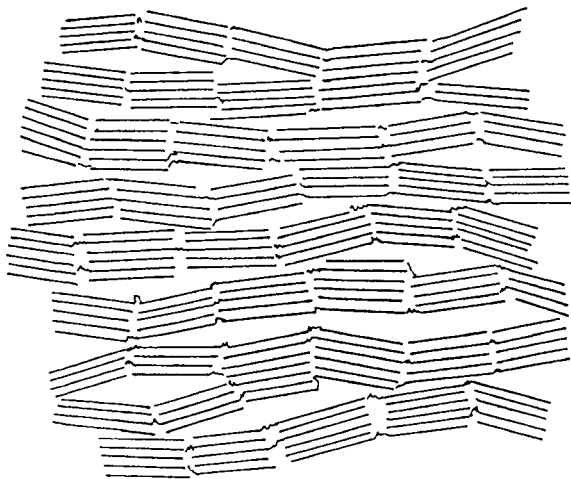
A short time later, in the same journal, Franklin published her first study of graphitisation.¹³ This was important work, because it was the first such study to include heat treatments up to 3000°C. Earlier studies, such as those of H. L. Riley and colleagues at Newcastle,¹⁴ had been hampered by the lack of laboratory scale furnaces capable of reaching these temperatures. After the war, however, the demand for large quantities of synthetic graphite for use in nuclear research led to a renewed interest in graphitisation. As a result, the first small scale induction furnaces capable of achieving temperatures of 3000°C and above were developed. Franklin was fortunate in having access to one of these, at the French Laboratoire de Haute Temperature. In her paper, she began by describing the XRD patterns of carbons prepared at about 1000–1500°C in an atmosphere of argon. The interplanar (002) spacings were all found to be very close to 3.44 Å. She then carried out further heat treatments up to 3000°C, and found that the spacings fall to approximately 3.354 Å, the value for single crystal graphite. This fall in the interplanar spacing is associated with a change from a 'turbostratic' structure, in which the planes are rotated randomly with respect to each other, to the perfect ABA structure shown in Fig. 2. Franklin believed that graphitic carbons could *only* have interlayer spacings of 3.44 or 3.354 Å, and that measured values which fell between these two showed that the sample contained phases of perfect graphite interspersed with regions of turbostratic structure (it still seems to be unclear whether this is the case, or whether graphite can exhibit a whole range of intermediate spacings). She used the shape of the (112) line to determine the proportion of layers which were oriented 'correctly', and showed that the relationship $d = 3.440 - 0.086(1 - p^2)$ existed between interlayer spacing d in Ångstroms and the proportion of disoriented layers p . This expression is still widely used today to estimate the degree of perfection of a graphitic carbon from measurements of the d spacing.

Graphitising and non-graphitising carbons

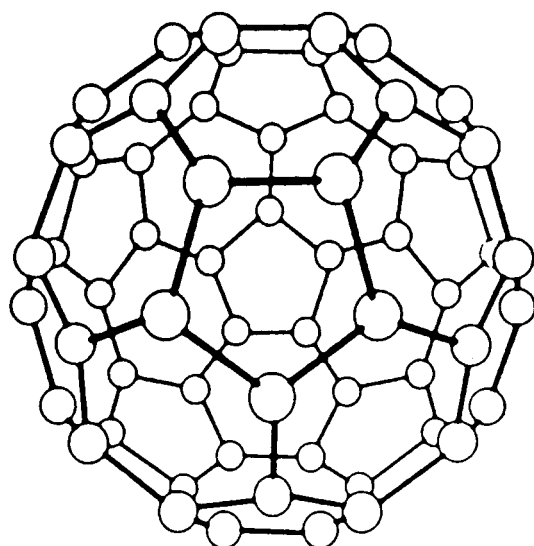
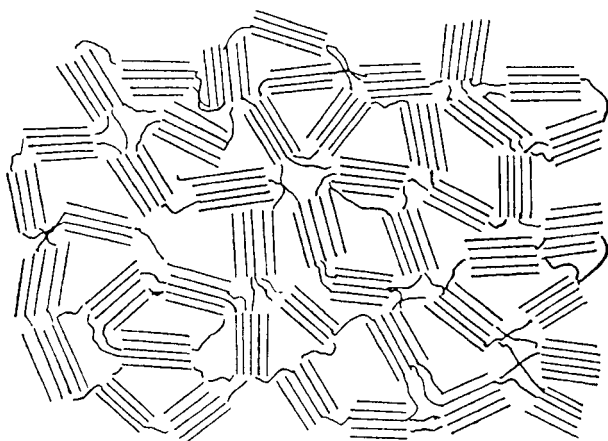
Undoubtedly Franklin's most important contribution to carbon science was her demonstration that carbons prepared by the pyrolysis of organic materials fall into two distinct classes, which she christened graphitising and non-graphitising. This work was an extension of her previous studies of graphitisation. Using the induction furnace, she carried out a series of heat treatments on a range of organic precursors at temperatures up to 3000°C. It would be expected that these very high temperature treatments would convert the disordered carbons into crystalline graphite, which is known to be the most thermodynamically stable form of solid carbon. But Franklin's results showed otherwise: while the cokes could be graphitised by heat treatments above about 2200°C, the chars could not be transformed into crystalline graphite, even at 3000°C. Instead, they formed a porous, isotropic material which only contained tiny domains of graphitelike structure. These results demonstrated for the first time the key distinction between cokes and chars.

Franklin summarised her studies of graphitisation in a lengthy paper for *Proceedings of the Royal Society*, published in 1951, which is one of the classics of the carbon literature.¹⁵ In this paper she coined the terms graphitising carbons and non-graphitising carbons to describe the two classes of material she had identified, and proposed models for their microstructures (shown in Fig. 3). In these models, the basic units are small graphitic crystallites containing a few layer planes, which are joined together by cross-links. The structural units in a graphitising carbon are approximately parallel to each other, and the links between adjacent units are assumed to be weak (as in the upper part of Fig. 3). The transformation of such a structure into crystalline graphite would be expected to be relatively facile. By contrast, the structural units in non-graphitising carbons are oriented randomly (Fig. 3, below), and the cross-links are sufficiently strong to impede movement of the layers into a more parallel arrangement. Although these models do not represent a complete description of graphitising and non-graphitising carbons, since the precise nature of the cross-links is not specified, they provided for many years the best structural models available for these materials.

Today, the distinction between graphitising and non-graphitising carbons remains incompletely understood. In particular, the atomic structure of chars and the reason for their resistance to graphitisation has never been clearly established. There is a growing feeling, however, that the key to the problem may lie in the discovery of a new class of carbons known as fullerenes. Fullerenes are a group of closed cage carbon particles of which the archetype is buckminsterfullerene, C₆₀, whose structure is shown in Fig. 4. They were first identified in 1985 by Harry Kroto, of the University of Sussex, and Richard

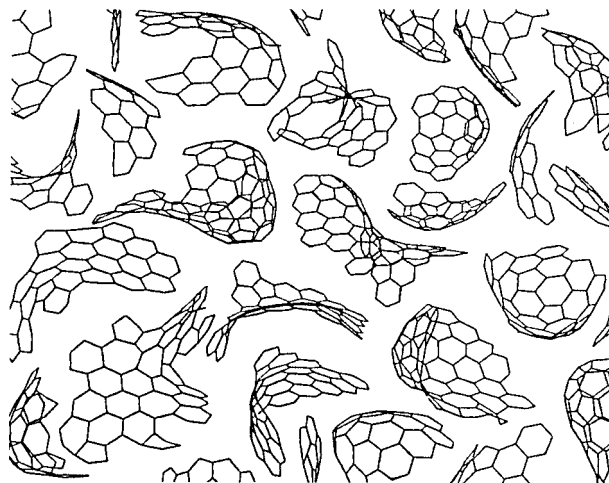


3 Franklin's representations of graphitising (above) and non-graphitising carbons



4 Buckminsterfullerene, C₆₀

Smalley, of Rice University, Houston, and their colleagues, during experiments on the laser vaporisation of graphite.¹⁶ Subsequently it was found that they could be prepared in bulk using a simple carbon arc, and this stimulated a deluge of research which led to the discovery of a whole range of new fullerene related carbon materials including nanoparticles and



5 Model of the structure of non-graphitising carbons based on fullerene-like elements

nanotubes.¹⁷ The distinguishing structural feature of these new carbons is that they contain pentagonal rings in addition to hexagons. These pentagons produce curvature, and Euler's law states that the inclusion of precisely twelve pentagons into such a lattice will produce a closed structure.

The discovery that carbon structures containing pentagons can be highly stable led to speculation that such structures might be present in well known forms of carbon. At first, this speculation centred on soot particles, whose spheroidal shapes immediately suggest a possible link with fullerenes. However, there is also growing evidence that microporous carbons may contain fullerene-like elements. The first indication of this came in a high resolution electron microscopy study¹⁸ published in 1997. In this work, non-graphitising carbons prepared from polyvinylidene chloride and sucrose were heat treated at temperatures up to 2600°C. It was found that the high temperature heat treatments produced a structure made up of curved and faceted graphitic layer planes, including closed carbon nanoparticles, which were apparently fullerene-like in structure. This suggested that fullerene-like elements may have been present in the original carbons, and subsequent studies using a variety of techniques have provided support for this idea. Eiji Osawa and colleagues at the Toyohashi University of Technology in Japan have also demonstrated that C₆₀ can be extracted from wood charcoal.¹⁹ As a result of these studies, many workers in the field now believe that charcoal has a structure made up of fragments of randomly curved carbon sheets, containing pentagonal and heptagonal rings dispersed throughout a hexagonal network, as shown in Fig. 5. However, this idea is by no means universally accepted.

Relevance of carbon research to later work

When she moved to King's College London in 1951, Rosalind Franklin knew little biology and had never

carried out X-ray crystallography on single crystal samples. In some ways, however, her work on carbon provided a valuable background for her biological research. Her studies of the density of coals would have been useful when she came to make density measurements on DNA, measurements which proved crucial in elucidating the structure, while the X-ray diffraction work would have given her some useful experience of this technique. It should be recognised, however, that the X-ray diffraction study of carbons was generally much less demanding than her later work on DNA. The carbon work was carried out using powder samples, and therefore involved none of the difficulties associated with preparing and mounting single crystal samples, and the interpretation of the results was also much more straightforward. In the case of the carbons we have a disordered, polycrystalline structure whose diffraction patterns consist of diffuse rings or bands. To interpret these patterns, Franklin began by assuming a simple structure consisting of a single graphite sheet, and then computed the theoretical diffraction pattern using the Fourier method. Comparison of the computed and experimental patterns then enabled her to draw some basic structural inferences about the carbon sample. For DNA or any other large molecule the situation is very different. Here we have a complex but well defined structure which gives a diffraction pattern consisting of discrete spots or arcs. This cannot be interpreted directly using Fourier methods because of the phase problem. Instead, Franklin attempted to solve the structure using the Patterson method, an extremely laborious process used in the days before electronic computers. Ultimately, of course, the structure was not solved in this way, but through the model building exercises of Watson and Crick.

Conclusion

In his obituary, J. D. Bernal stated that ‘as a scientist Miss Franklin was distinguished by extreme clarity and perfection in everything she undertook’,² and this certainly applies to her work on carbon. Working with recalcitrant materials, she was able to achieve fundamental results through a combination of clear-sightedness, determination, and experimental skill. It is sometimes said that her work was important in the development of carbon fibres and in the nuclear industry, but it would be misleading to say that it had any enormous commercial impact. Instead, her studies provided us with new and fundamental insights into the nature of carbon, the most important of all elements.

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Peter Harris was brought up in Gloucestershire and read chemistry at Birmingham University. He went on to study for a doctorate at Oxford University, working on transmission electron microscopy of catalytic materials. Since then his research has focused on the application of various forms of microscopy to problems in solid state chemistry and materials science. He carried out postdoctoral work at both Cambridge and Oxford universities, and currently works in the Chemistry Department at Reading University, where he is responsible for electron microscopy. He has published over forty scientific papers, and his book 'Carbon nanotubes and related structures – new materials for the twenty-first century' was published by Cambridge University Press in 1999.
