

Carbon-based Solids and Materials

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Pierre Delhaes

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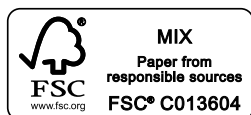


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Introduction

The carbon atom is an essential building block in nature; it is at the origin of life on our planet especially because of the complexity of its chemical bonds. It can also self-assemble in different ways producing numerous solids and materials. Although some have been known for a long time, such as diamond and natural graphite, research in the last 50 years has uncovered other new materials reported as polymorphs. These significant advances constitute an example of the mutually beneficial exchange between science and technology. The rate of knowledge expansion on this topic has sometimes led both researchers and engineers to think that some discoveries were made several times. Hence, we decided to integrate the most recent advances historically, and this was the driving force behind the preparation of this book. To achieve this, the book has been divided into three parts. The first presents five chapters focusing on the allotropic forms of carbon, including their precursors and closely related analogs. The second part focuses on their intrinsic properties, and the third describes the applications of carbon-based materials. The themes and contents are summarized in the table of contents. In the first part (Chapters 1 to 5), we define and describe natural forms of carbon, referring in particular to the allotropes of graphite and diamond, as they are the basis of the newly discovered molecular phases, which include carbynes, fullerenes, and planar or rolled-up graphene sheets. This part is based on thermodynamic and structural characteristics of these phases and is further developed based on concepts borrowed from solid-state physics. Later, the comparison of properties between polymorphic varieties is reported (Chapters 6 to 10) according to a solid-state physics approach. Finally, the last part focuses on materials, introducing the physical chemistry of surfaces and interfaces when exposed to their environment (Chapters 11 to 15). These materials, which are the result of human development, were created to exploit a physical property or specific chemical functionality corresponding directly to the

desired application. We will demonstrate that this area of material science is highly dependent on the evolution of our society and its economy including the current developments of nanosciences and nanotechnologies.

The structure of this section is based on a historical approach that integrates several key references used throughout the whole book. The full list of general references is provided at the end of this introduction; it appears in chronological order commencing with the book by Henry Le Chatelier, which was published more than a century ago and pioneered the description of the different carbon-based phases. The collective manuscript on carbons, published in the 1960s in France has been a benchmark ever since. However, recent developments, in particular the case of the new molecular phases and their properties, have instigated the requirement for new research in order to describe them appropriately. Some theoretical reminders on physics of the solid can be found in various sections, as well as descriptions of the most relevant characterization techniques associated. Thus, in this well of knowledge containing “theory-technique-subject” we have focused on solids and carbon-based materials. It is suggested that the interested reader complement this with a list of less specialized books and websites (see for example Wikipedia online).

In terms of nomenclature we adopted the terminology recommended by IUPAC (E. Fitzer, K.H. Kochling, H.P. Boehm and H. Marsh, publication DKG n° 32, 1998). The main abbreviations and symbols as well as the keywords used are listed in two different indexes. Moreover, in each chapter the most recent and historically significant publications are listed in an effort to highlight the progress in each field of interest. A non-exhaustive and highly subjective approach has been employed in order to establish a classification based on the different varieties of carbon instead of developing each specific property. Finally, we have decided not to highlight the diverse utilizations and industrial applications of these materials (no reference to any patent), which are in constant evolution, but instead to provide an overview of the basic notions used and their evolution with time.

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This book results from several years of work and its conception and preparation was made possible thanks to the help and cooperation of many colleagues and friends. It has to be considered as the fruit of half a century of research on carbons at the “Centre de recherche Paul Pascal” (Centre National de la Recherche Scientifique et Université de Bordeaux). It is dedicated in memory of the pioneering works on

carbon materials started in the sixties by Adolphe Pacault and André Marchand at Bordeaux. The influence of the scientific community belonging to the French carbon group has also been tremendous with its annual meeting where exchanges and discussions are always intense.

Concerning the manuscript preparation I am deeply grateful to Michel Trinquecoste and Stéphane Reculosa for the illustrations, then to Nicolas Nouvel for the English translation which has been updated and improved, correcting some mistakes present in the French edition. I finally dedicate this book to my wife Christiane Delhaes, our children and grandchildren, who have kindly followed all the steps of this project.

General bibliography

Below is a list of books that are fundamental references for the work described in this manuscript.

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PART 1

Carbon Phases, Precursors and Parent
Compounds

Chapter 1

A Historical Overview

Carbon is a special element in the periodic table; it is not abundant on Earth with only 0.2% of the total mass of our planet being composed of carbon, but its role is nevertheless fundamental. As described by P. Levi [LEV 95], carbon can form bonds with other light elements and with itself, laying the foundation on which chemistry and biology have been developed, and ultimately allowing the miracle of life to happen. We will focus on its ability to bind with itself in different ways, leading to various solids, both natural and artificial. It is worth mentioning that carbon-based materials were and still are the main source of energy utilized by mankind. First, we will consider these materials as the result of human activities, sort of corollary to the evolution the human race, related to each period of time and representative of each successive civilization. In the following presentation, natural carbon-based materials, both from Earth or with a cosmic origin, will be defined and presented. These materials, having been present through the creation of our universe, effectively bridge the gap between astrophysics and geophysics. We will also demonstrate the existence of similarities in both natural and artificial carbon-based materials, as they constitute an important source of information, by showing that there is no real limitation or barrier from one category to the other. Finally, this overview will be completed by the contribution of quantum mechanics over the past hundred years, which opened the way to the current representation of all varieties of known carbons.

1.1. The alchemy of carbon

Coal derived from animal or plants was the first source of carbon utilized by mankind as a result of mastering fire. The word “carbon” comes from the Latin

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“*carbo*” meaning coal, which is the natural product obtained from the controlled combustion of vegetal matter. Evidence of its first utilization appears in the parietal art of Cro-Magnon man in the Lascaux caves in Dordogne, France, painted some 15,000 years BC [VAL 00], (see section 1.5.5.4 on C¹⁴ dating).

During prehistoric times coal was utilized as a source of combustible material as a reducing agent for metals. Approximately 4,000 years BC in the Middle East, ovens capable of melting ores and reducing copper oxide were built using wood coal as the main combustible. Certainly, unexpectedly, a combustion chamber using a reducing atmosphere was built and later controlled. In this context, copper was the first metal to be exploited and utilized, leading to the bronze age.

Starting from this discovery, other metals were isolated. A remarkable case is iron produced during the reduction of iron oxide; this is not straightforward because, unlike copper, metallic iron is not stable and naturally converts into carbides, such as cementite, whose formation control was achieved empirically. Historians have agreed to attribute this invention to the Hittites approximately 1,500 years BC, which presents a millstone for both agriculture and the art of conflict [MOH 90] and was followed by technical progress in metallurgy.

During antiquity, the great civilizations developed applications of metallurgy in various areas, which strongly influenced subsequent developments up to this day. For example, Egyptians used coal prepared from plants as a remedy for gastric problems, relying empirically on its property for great absorbance and natural selectivity, charcoal was utilized as a pigment for make-up (called “*khôl*”) and also for tattoos, but also as the main constituent of bitumen used to prepare mummies [VID 90].

The Chinese have used coal in various mixtures, especially in Chinese ink and for the preparation of the black powder [TEM 00]. The black ink was made of a colloidal suspension of charcoal and has been used since 2,500 years BC for writing, calligraphy, and painting on both paper and silk. The constituents of the black powder are potassium nitrate, sulfur, and coal.

Around 850 AD, Taoist monks developed a formulation of black powder similar to the one used nowadays and developed pyrotechnic applications and its explosive property. From that time onwards, the development of firearms, from rifles to canons, occurred first in Asia then spread to Europe in the Middle Ages (12th and 13th centuries) via the Arabs, changing military techniques worldwide. This invention is a significant outcome of the development of alchemy [BRI 99]; a science developed by the Arab civilization based on the Greek heritage, incorporating the discoveries made in Asia, and later brought to Europe, often through conflict.

1.2. Elemental carbon and its allotropic varieties

The fundamental understanding that preceded the birth of chemistry was the concept of the smallest elemental particles, also called atoms, which was laid out by the Greeks more than 25 centuries ago. The scientific work undertaken in western Europe during the 16th and 17th centuries slowly converged towards the creation of modern chemistry with the definition of atoms described nowadays. This new science evolved from the original work of Antoine Laurent Lavoisier and the publication of his dissertation in 1789 entitled *Traité élémentaire de chimie présenté dans un ordre nouveau et d'après les découvertes modernes* [LAV 89]. In Figure 1.1 we have reproduced the table of simple substances established by Lavoisier where the word “*carbone*” appears in the non-metallic substances in front of its earlier name “*charbon pur*”.

By studying this table, where chemical elements lay next to “light” and “calories”, it can be clearly seen how difficult it has been to achieve a rational classification. This essential yet tedious work was accomplished by a large number of chemists in the 19th century with the implementation of symbols to represent chemical reactions. In addition, the attribution of atomic masses associated with these reactions was a key development instigated by J. Dalton in 1808 [DAL 08]. It is only at the end of the century that the periodic table was elaborated by Mendeleev (77 elements were included in 1889) and accepted by the chemist community.

Returning to elemental carbon, it is worth mentioning that the identification of all natural forms was a slow process that took place in the 19th century. Two crystalline allotropes extracted from mines have been known for a long time: graphite (from the Greek *grapho*) and diamond (*adamas*), both of which consist primarily of carbon. Comparing diamond’s extreme hardness and its transparency to the easily cleaved graphite and its shiny black color, the fact that they share a common composition was not obvious. Previously they were compared and sometimes confused with quartz and molybdenite, respectively. The history of diamond as a precious stone seems to start in India during antiquity prior to reaching Europe. It was already mentioned during the 4th century BC in a manuscript written in Sanskrit, and it is interesting to note that the oldest printed book was named *Diamond Sutra*, apparently made in China in the 9th century AD (currently kept at the British museum in London). Much later, Marco Polo described in the documentation of his travels [NEW 50] the use of diamond in China for parures. Finally, the experiment of Sir H. Davy in 1814 is noteworthy, in which he burnt his wife’s diamonds to confirm that the amount of carbon dioxide formed is equivalent to that obtained from coal or graphite [NEW 50]!

	Noms nouveaux.	Noms anciens correspondans.
	Lumière.....	Lumière.
		Chaleur.
		Principe de la chaleur.
	Calorique.....	Fluide igné.
		Feu.
		Matière du feu & de la chaleur.
		Air déphlogistiqué.
	Oxygène.....	Air empiréal.
		Air vital.
		Parte de l'air vital.
		Gaz phlogistiqué.
	Azote.....	Mofete.
		Base de la mofete.
	Hydrogène.....	Gaz inflammable.
		Base du gaz inflammable.
	Soufre.....	Soufre.
	Phosphore.....	Phosphore.
	Carbone.....	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique..	Inconnu.
	Radical boracique..	Inconnu.
	Antimoine.....	Antimoine.
	Argent.....	Argent.
	Arsenic.....	Arsenic.
	Bismuth.....	Bismuth.
	Cobalt.....	Cobalt.
	Cuivre.....	Cuivre.
	Étain.....	Étain.
	Fer.....	Fer.
	Manganèse.....	Manganèse.
	Mercure.....	Mercure.
	Molybdène.....	Molybdène.
	Nickel.....	Nickel.
	Or.....	Or.
	Platine.....	Platine.
	Plomb.....	Plomb.
	Tungstène.....	Tungstène.
	Zinc.....	Zinc.
	Chaux.....	Terre calcaire, chaux.
	Magnésie.....	Magnésie, base du sel d'Épſom.
	Baryte.....	Barote, terre pesante.
	Alumine.....	Argile, terre de l'alun, base de l'alun.
	Silice.....	Terre ſiliceuſe, terre vitrifiable.

Figure 1.1. Table of simple substances proposed by A.L. Lavoisier in his book entitled *Traité élémentaire de chimie* in 1789 [LAV 89]

During this same century the concept of allotropy (*allos tropos* in Greek), was introduced by Berzelius around 1840 which described the different physical properties that can be obtained from a pure substance. This concept and its corollary describing the structure (polymorphism) seemed to have appeared for the first time in the work of Mitscherlich starting in 1822 [MIS 22], [MIS 23]. An overview of the situation at the beginning of the 20th century is provided by the book of Henry Le Chatelier, *Leçons sur le carbone* (Le Chatelier, 1908). In the second chapter on physical properties we can read the following:

“*Le carbone non combiné se présente sous des formes très curieuses: carbone amorphe, graphite et diamant.*” (pure carbon is present in very curious forms: amorphous carbon, graphite and diamond)

Following the discovery of X-rays by W.H. and W.L. Bragg in 1913 [BRA 13], these authors identified the cubic structure of diamond and, several years later, Hassel and Mark [HAS 24], and simultaneously Bernal [BER 24], discovered the structure of hexagonal graphite. In addition to these crystalline phases, Le Chatelier mentioned an amorphous carbon, which is the general name for all graphite-like carbons, from natural sources (coal mine and other carbon-rich sediments) or synthetic carbons, such as charcoal obtained by a controlled combustion under the influence of temperature. An organic substance is decomposed by the thermal process known as pyrolysis under a controlled atmosphere, by temperature in the range of 500-700°C leading to carbon-based residues or by the carbonization process at higher temperatures (typically going from 700° to 1,500-2,000°C). The study of structure associated with the development of X-ray diffraction of these non-crystalline carbons mainly occurred in the middle of the 20th century ([WAR 41], [FRA 50], [FRA 51]). There are studies of the graphitization process, such as a progressive crystallization into graphite, sometimes an incomplete process, by thermal treatment above 2,000°C (*Les carbonées*, Volume 1, Chapter 1, 1963). Consequently, research on the ideal conditions to obtain these non-crystalline forms, their characterizations, and applications as carbon-based materials were a great source of interest in the last century, as the associated developments were strongly related to the successive industrial changes that have shaped our contemporary societies.

1.3. Novel molecular varieties

After World War II, and in the second half of the 20th century, the exponential development in scientific research led to huge advances in the science of carbon with the discovery of new and unexpected structures (presented in Figure 1.2). Focusing on the main events, it is necessary to first mention the unsuccessful