# **History of Carbon**

# **Introductory Remarks**

Carbon compounds are rather prominent on this planet. They are called **organic compounds** and are found in abundance in what's called "biology". For example, the following three simple and well-liked molecules contain plenty of carbon (C):

- C<sub>2</sub>H<sub>5</sub>OH. Chemical short-hand for the (ethylene) alcohol found in beer, red wine and other important liquids.
- C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. Known as *starch* and found, for example, in pasta and other necessities of life.
- C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>. Sweetening life because it's (glucose) sugar.
- There are a hell of a lot (million, billion, trillion, whatever you like) more organic molecules around, including DNA and other rather complex stuff. Pretty much all of them could be used to make carbon. We also have carbon compounds in gases like the carbon dioxide (CO<sub>2</sub>) that provides the fizz in soda and changes the climate, or carbon monoxide (CO) that kills you and allows (carbon) smelting of metal ores.
- Elemental carbon, however, is not so easy to find. Ancient humans pretty much only encountered it in the cinder, soot, and charcoal leftovers found after some tree was hit by lightning and burned down, or after they started to make fire themselves on a regular base (some 300,000 to 400,000 years ago; possibly even more than 1 Mio years). Whatever *black* stuff remains after a careless burning of organic material is very dirty carbon. The greyish stuff is ash, consisting of inorganic "salts".
- The name carbon comes from the the French "charbone", which in turn came from Latin "carbo", meaning "charcoal". In German the name is "Kohlenstoff" which literally means "coal-stuff".

Looking around today, we can find more or less elemental or natural carbon in the following modifications:

- Residues of (incomplete) burning as outlined above. The best you could do for producing pure carbon was to go for **charcoal** or **soot** deposited on some surface.
- Coal; coming in various grades from *lignite* with about 60 % 75 % carbon content to *anthracite* with > 91.5 % carbon content.
- Graphite, the hexagonal form of crystallized carbon.
- Diamond, the cubic metastable form of crystallized carbon.
- Synthesized or man-made carbon adds a few more versions; use this link for details.

The *History of Carbon* thus has several main and subsidiary branches:

- 1. The history of all its modifications *before* it was known that they all are just different expressions of the same element.
- 2. The history of figuring out what the element carbon can do after its nature became clear.
- 3. The history of the relation of carbon and iron.
- 4. The history of organic chemistry.
- 5. .....
- Let's start with the first branch.

# **History of Carbon Modifications**

#### Charcoal

Charcoal results when (dry) wood is heated to at least 275 °C (527 °F) in an oxygen-free environment. The wood then can't burn or oxidize with the basic reaction  $C + O_2 \rightarrow CO_2$  but **pyrolyzes** to carbon (in the form of charcoal) and various gases.

*Pyrolysis* is the fancy word for "thermochemical decomposition of stuff" or simply the falling apart of chemical compounds when you heat the stuff but don't supply oxygen for a proper burning. "Pyr" is Greek for "fire" and the root of the English word "**pyre**"; "lysis" is Greek for "separating" as in "electrolysis".

Chemically speaking, wood is mostly a mixture of cellulose (40% – 50%), hemicellulose (15% – 25%) and lignin (15% – 30%). Chemical formulae for that kind of stuff are, for example, (C<sub>6</sub>H<sub>10</sub>O <sub>5</sub>)<sub>n</sub> for polysaccharide cellulose, or C<sub>10</sub>H<sub>12</sub>O <sub>3</sub> for a lignin variant.

In other words: besides carbon (C) wood contains quite a bit of oxygen (O) and hydrogen (H). It is thus not surprising that the gases formed during pyrolysis are mostly carbon monoxide (CO), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). Note that the first three gases burn readily - if there is oxygen available.

Pyrolysis of pretty much all organic stuff (including you) thus can be done for several purposes:

- 1. Making *charcoal* needed for old-fashioned smelting or modern barbecuing from wood.
- 2. Making *coke* for modern smelting from coal.
- 3. Making combustible gases needed, e.g., for driving a car if no gasoline is around, from coal, wood, plants, waste, ....
- 4. Cleaning up organic waste including toxic and smelly stuff by turning it into coal and gases.
- 5. Turning old tires into coal / coke, diesel oil and combustible gases (then used for firing the plant).

The first two processes we will encounter more often in this Hyperscript, they relate directly to iron and sword making. The last two items are hot topics in our modern waste-producing American way-of-life world. Number 3 is now out of style but, believe it or not, was quite prominent in WW II Germany. Gasoline was scarce and cars and trucks had a "wood carburetor", or more precisely, an unwieldy gas generator for pyrolyzing wood, a feed tube for the gases, and a carburetor etc. adopted to feeding the gas to the engine. The picture below shows it all.

It wasn't much fun to run a wood-fueled car. But that was still far superior to not running a car at all. I guess that the urge for getting away on wheels is second only to <u>drinking beer</u>, which comes right after urge No.1.



Having decent charcoal around was important for millennia. Charcoal was decisive for:

- Smelting of metals from the ores.
- Melting of the smelted metals for casting.
- Forging of non-meltable iron and steel.
- Making glass and advanced pottery. This coul also be done with dry wood, hoever.
- If that list confuses you, turn to this module.

Charcoal making is relatively easy and was done in pretty much the same way for thousands of years. Wood is all that is needed. Northern Europe thus had no problem in this respect for quite a while, but ancient Egypt, for example, had not much wood at its disposal and was thus at a certain disadvantage concerning the charcoal-enabled technologies given above. On the other hand, they didn't need wood as urgently as my forebears to keep warm during the 9 months when it is cold.

Charcoal in the time-honored fashion is produced by pyrolyzing a pile of wood that is contained in an (almost) airtight enclosure made from mud bricks or stuff like that. Shoveling earth on the pile might already do the trick. Of course, the ignorant charburners and the important well-educated or at least rich people didn't call it "pyrolyzing" for the first few thousand years but "burning" because some (small) part of the wood is really burnt. For that you needed to have a few vents in the mud cover, and the initial burning proper produced the heat to get the pyrolysis going in the larger part of the pile.

The pictures below show what a charcoal pile looked like since about 1.400 AD. Before that, the wood was simply thrown into a pit in the earth, set on fire and then covered to prevent all-out burning.





As soon as the process has been started around 275 °C (527 °F), it is self-supporting since pyrolysis generates heat of its own and thus raises the temperature. The process continues until all the wood has been converted. As a rule of thumb, 5 tons of wood make 1 ton of charcoal.

Of course, since wood contains more stuff besides the major ingredients listed above, all the non-burnable stuff (called "**ashes**" in burning proper) is now contained as dirt in the charcoal. Have you ever wondered why flour (mostly starch) in Germany has always a number on it like "type 405" or "type 1050"? This number just gives the weight of the remaining ash in milligram (mg) if you burn 100 grams (g) of the flour. The more ash, the more minerals are in there. Ash generally accounts for 1 % or less of the weight of (dry) wood. For some odd reason my wife thinks that ash is good for you when she uses flour for baking.

Wood ashes consist mainly of oxides of calcium (Ca), potassium (K) and magnesium (Mg). These oxides account for roughly 80 % of the ash; next come oxides of aluminum (Al), phosphorous (P), sulfur (S) and a few more.

Charcoal retains the original cell structure of the wood and thus is very porous or, in other words, has a large surface-to-volume ratio. That's why it burns far better and hotter than wood or regular coal. There is simply more surface area where the process can take place; see below:



Of course, ever-present "**sympathetic magic**" was invoked to relate *hard* iron to charcoal made from *hard* wood and *soft* iron to charcoal from *soft* wood, etc. It is true to some extent that charcoal made from *hard* wood might make your iron hader, i.e having a higher carbon content - but no because of magic but for <u>good scientific</u> reasons. It was a good idea to be very concerned about the charcoal that you used in your smelter, and smelter operators had a strong tendency to never chane a "winning team".

When metal smelting became a major industry, let's say ever since 500 BC, de-forestation became a problem. Wood or charcoal had to be transported over ever increasing distances, and there is some speculation that the depletion of wood resources lead to the decline of whole empires, e.g. in Africa, (for example the famous Kingdom of Kush), where iron was smelted as early as 900 BC.

Charcoal burners or Charburners were a-plenty in ancient metal-working society but their profession usually had a somewhat seedy reputation. Of course, throughout most of history, the useless but powerful nobility looked down on manual labor anyway, and the appearance of always black and dirty charburners did not particularly recommend them as good companions.

#### Diamond

In a few areas around the globe raw diamonds could be found just so; in particular, it appears, in deposits of some Indian rivers. Diamonds have been known in India for at least 3,000 years, maybe even 6.000 years. What exactly people did with them is unclear. They were used as (uncut) **gemstones**, religious icons (whatever that might be) and as tools for scratching and working hard things.

The name diamond (German: Diamant), you guessed it, derives from the ancient Greek "adámas", meaning "proper", "unalterable", "unbreakable", and so on. I would guess that it is the same root as "atomos", meaning indivisible or uncuttable, which gave us the "atom" - but it is all Greek to me.

Diamonds have a simple <u>cubic face-centered</u> (fcc) structure like silicon (Si) or germanium (Ge) as shown below.



Blue and green spheres mark the position of carbon atoms, the blue spheres mark also the position of lattice points. Red lines show the bonds between atoms. The black lines are <u>meaningless</u>, they just guide the eye to identify the cubic structure.

A Chinese work from the 3rd century BC refers to diamonds as amulets of foreigners (warding off evil influences) while the Chinese themselves used (imported) diamonds as tools for working <u>jade</u>. While diamonds for millennia came mostly from India, Brazil (major finds in 1725) and South Africa (major finds 1867 in Kimberley) eventually took over.

Small numbers of diamonds began appearing in European jewelry in the 13th century; they were used as "accent points" among <u>pearls</u> set in gold. Louis IX of France (13th century) reserved diamonds for the king by law, demonstrating that this piece of carbon was now seen as extremely valuable. The <u>big days of diamond</u>, lasting until today, started when the facetted cut that we have today as a matter of course was invented by Jules Cardinal Mazarin in the 17th century.

Diamonds are a <u>metastable phase</u> of carbon; the stable phase is hexagonal graphite. The formation of diamonds therefore requires very specific conditions: rather high pressure (around 5 GPa) and high but not excessively high temperatures (around 1.000 °C). That makes it rather difficult to grow big single diamond crystals in the laboratory. On the other hand, making small diamonds or coating all kinds of materials with a thin layer of diamond is now commercial routine.

The black stuff left in your oven, after doing your turkey or whatever, contains what one could call "amorphous diamond" with a lot of strong diamond-like bonds. It is thus not surprising that this annoying matter is very hard and durable and almost impossible to scratch off or to dissolve in chemicals that don't tend to kill you on the side.

#### **Coal and Coke**

**Coal** is the black stuff we dig out of the ground in ever increasing quantities. The table below lists the 8 biggest producers; there are of course many more.

Country	2009	2011
	Mio tons	
China	2.971	3.162
USA	985	997
India	571	571
Australia	399	420
Indonesia	301	336
Russia	297	324
South Africa	247	255
Poland	134	135
Total	5.905	6.200

Most of that coal ends up as carbon dioxide (CO<sub>2</sub>). Frightening, isn't it? A lot of this is used to produce the - roughly - 1.200 Mio tons of steel per year.

In some areas of the world coal seams came out of the ground, and coal then was just dug out and used on a small scale, e.g. by the Romans. Wikipedia writes: "In Roman Britain, the Romans were exploiting all major coalfields (save those of North and South Staffordshire) by the late 2nd century AD. While much of its use remained local, a lively trade developed along the North Sea coast supplying coal to Yorkshire and London. This also extended to the continental Rhineland, where bituminous coal was already used for the smelting of iron ore."

I can't quite believe that. Smelting iron ore with bituminous coal, or any coal for that matter, would generate very inferior steel because of the sulfur problem. My guess is that smelting and melting have been confused <u>once more</u>. Major use of coal started when Great Britain had finally cut down most of its forests in the 16th century. The use of coal as domestic fuel rapidly expanded, as did the diseases caused by the smoke. The industrial revolution in the 19th century finally led to an explosive growth of coal mining that has essentially continued to this very day.



Coal, mind you, is *not* a well defined substance and it is *not* carbon as already pointed out <u>above</u>. In the best case (**anthracite**) it contains about 10 % foreign matter, in the worst case (lignite), dirt accounts for around 40 %. The non-coal stuff contains mostly oxygen and hydrogen. But *all* grades of coal, unfortunately, contain about 1 % of sulfur, and that is rather bad for steel production, not to mention the environment (look up "acid rain"). The figure below gives a schematic view of the composition of coal.



If there would only be ordered arrays of those hexagons, it would be pure graphite. Wherever two lines meet in the upper picture sits a carbon atom and a hydrogen atom (mostly not drawn). Where three lines meet is only a carbon atom.

**Coke** (short for "coal-cake"), is to coal what wine is to grapes: a highly refined and superior product in comparison to the raw material it was made from. One could also say that it relates to coal the same way charcoal relates to wood. Coke here, to be perfectly clear, is *not* something you snort up your nose.

In a nutshell: coke results when you <u>pyrolyze</u> coal. Rather pure carbon is left over, and as a by-product **coal-gas**, and coal-tar are produced in large quantities. These by-products created their own industries. Coal gas (also called **town gas** and illumination gas) was the primary source of gaseous fuel for lighting, cooking and heating in many cities in the 18th and 19th century. Coal tar was used for making all kinds of early organic compounds like creosote.

In the western world, **Sir Hugh Plat** (1552–1608), an English writer and inventor, first suggested the process in 1603. Nobody heeded his idea, of course, until the need to have something that could replace charcoal became a matter of life and death. Charcoal was becoming expensive in merry old England in the 16th century because the forests were mostly cut down by then, and that meant that metal smelting became expensive. Well, yes, but who cares?

Far worse was that **beer brewing** and thus beer became expensive, because you need a good fuel to roast the malt needed for making beer! You just can't run a decent civilization that smelts metals and is bent on <u>conquering</u> the world (or at least the French) without large quantities of good and affordable beer, as I have <u>ascertained</u> <u>before</u>. Using coal for roasting the malt impairs a foul taste to the beer because of the sulfur in the coal. Making coke became imperative, and beer brewing with coke started 1642 in Derbyshire for good.

Of course, after the bulk supply of beer was ensured, coke could then also be used to smelt metals, make swords and later guns, and all the other hardware needed for conquering the world. It took a while, however. It was not before 1710 that one **Abraham Darby** (1678 – 1717) developed a method of producing cast iron in a blast furnace fuelled by *coke* rather than charcoal. It took even longer before that caught on - only around 1800

pretty much all blast furnaces were run on coke. Some charcoal fanatics, however, where not convinced even then and kept their <u>smelters on charcoal</u> well into the 20th century

The <u>Chinese</u> did it the wrong way around. They started to make coke already in the 9th century AD but didn't use it for making first beer and then iron. They somehow got confused and started smelting iron with coke right away. In the 11th century they had a major iron industry running that was based on coke and not just charcoal. That kept them so busy that they never got around to making decent beer.

Poor suckers, it was downhill ever since. They could have conquered the world quite easily in the 15th century, long before the Spaniards and Portuguese made their bid, because they had superior hardware and ships, and many other advanced things like live-in concubines. Fortunately (for us), they didn't have the balls beer needed for some conquering. Now look at the British and the Germans. They focussed on beer for quite a while - and the British eventually did conquer most of the world and they still feel good about that! We Germans weren't quite that successful but at least we tried. The Americans today have some success, but their conquering-the-world efforts get rather mixed reviews. I blame it on the quality of their beer.

#### Graphite

Graphite is the stable phase of carbon with a <u>hexagonal lattice</u>. It is not a simple <u>hexagonal close-packed</u> structure but a bit more complicated as shown below.



The bonds *in* the hexagonal plane are very strong just like in diamond, while the bonds *between* the planes are very weak. That's why it is very easy to deform graphite in directions parallel to the hexagonal planes and very difficult in directions perpendicular to it. That allows applications that are breathtakingly different:

- Use poly-crystalline graphite. Whenever you press or pull on it, some areas shift easily and stick to the contact material. This is great for making pencils or lubricants.
- Use monocrystalline graphite in long fibres oriented in the hexagonal plane. When you pull at the fibres, you are trying to break diamond bonds and that is tough to do. Now protect your fibres from forces at right angles by encasing them in some epoxy. Bingo! You have made carbon-fiber-reinforced polymer or plastic (CFRP or CRP) with a strength-to-weight ratio that exceeds the best steels by far.

The name "**graphite** " was coined by one **Abraham Gottlob Werner** in 1789 from (what else?) ancient Greek: "grapho" = to draw, to write, because it was used in "lead" <u>pencils</u>. This already gives a hint that there was some confusion as to the nature of the stuff in pencils. People thought for a long time that natural graphite was some lead mineral.

Graphite is quite essential to modern technology. It is not only good for pencils, as a lubricant, or for CFRP; it is an electrical conductor that can take enormous temperatures (it doesn't melt but becomes directly gaseous around 3.750 °C (6780 °F) *and* is chemically very stable. That's why it is used in the high-temperature "electro" <u>smelting of difficult elements</u> like silicon.

Graphite may be considered as the highest grade of coal (above <u>anthracite</u>) and therefore is found in small quantities wherever coal is found. It was used pretty much throughout history as "black paint", it seems, e.g. on pottery. Personally, I'm not sure if the graphite paint found on old pottery resulted from using "true" graphite or just soot. After firing the pots, the result could be about the same.

Graphite proper came into its own after a huge deposit of extremely pure and soft stuff was discovered in 1565 (or possibly somewhat earlier) in the Borrowdale parish, Cumbria, England. The local yokels used it for marking sheep and probably didn't worry much about what that soft black stuff actually could be. A somewhat more advanced use coming up a bit later was to line the molds for cannon balls with this graphite, resulting in rounder, smoother balls that could be fired farther.

The military guys did wonder about what that useful black stuff could be, and promptly confused it with lead or some of the more common lead ores like <u>galena</u>. That is why graphite was known for a long time as "lead" or "**plumbago**" (based on the Latin "plumbum" for lead). This error survived to some extent up to the present day. In German, a pencil is still called "Bleistift", literally "lead pen". Archeologists also <u>confused lead and lead ore</u>. Granted that graphite, lead and galena *look* similar, one could at least distinguish graphite from the two others easily because the difference in (specific) weight is rather obvious, you might think. Yes, but to everybody before - roughly - 1750, the notion of chemical elements was unknow. Things that were similar were thought to be about the same. The differences were assigned to the presence or absence of "vital juices", "spirits" or "priciples" of this or that. Graphite in many aspects is far more similar to lead or lead ore then to diamond, or soot. I'm quite sure that even today it would be far easier to persuade most people that graphite is related to lead and not to diamond.

#### Soot and Carbon Black

**Soot** is that fine black stuff that remains in the air from burning something, and that the chimney sweep takes out of your chimney on a regular base. You only can avoid it in very "clean" fires. It results from the "incomplete combustion of a hydrocarbon", for example when a candle burns wax. Put a glass plate over a candle flame and you catch the soot in the air. It is part of what we call "smoke" and accounts for a lot of sick people, especially in countries where open fires are the standard for cooking.

Soot consists of rather small (below 100 nm) particles of carbon (plus some dirt). This particles might agglomerate to some extent, forming chains and God knows what, and at least parts of them consist of amorphous carbon. I'm sure, however, that you will find all other forms of carbon too, if you search long enough.



Soot, made *unintentionally* by you via burning something, should not be confused with **carbon black** that is made *intentionally* (by burning something). *Carbon black* is rather pure carbon that serves as raw material for important carbon-based products. It is, for example, used as pigment in your toner cartridge, and it is what makes care tires black. World production is around 10 Mio. tons a year. Make it very hot and it graphitizes as shown above. And don't confuse "carbon black" with *Black Carbon* - look it up yourself!

Ancient man used soot for painting himself, for tattooing, painting caves, whatever. It was not High-Tech and thus is not very interesting to us.

Modern man like me and my colleagues used very pure carbon black for a while in experiments designed to make very pure silicon via "<u>electro-smelting of difficult elements</u>". That also needed very clean silicon dioxide (SiO<sub>2</sub>). It didn't really work but that is another story. Working with the stuff makes everything (including you) quite black, too. I have never done anything quite that dirty again during my career, and that includes convincing my kids that the shortcuts I proposed on major hikes would bring us home pronto, not to mention running a major university faculty as Dean.

## **History of Putting Things Together**

#### It's Carbon!

You must admit that anybody not familiar with the basics of chemistry and the <u>periodic table</u> would declare you to be completely nuts if you would propose that all the stuff described above is one and the same basic substance. Before about 1700, "anybody not familiar" and so on would simply have been everybody minus a handful of fledgling scientists.

- It was Robert Boyle who suspected in 1661 that there were more than just the four classical elements that the ancients had postulated. He endorsed the view of elements as the undecomposable constituents of material bodies and made a distinction between mixtures and compounds. Nevertheless, he was also an alchemist (and a racist) and believed in the transmutation of metals making gold from lead, in other words.
- Antoine Lavoisier, the "father of modern chemistry" whom we have <u>encountered before</u>, supplied the first list of elements in his "Traité élémentaire de chimie (Elementary Treatise on Chemistry) in 1789. Oxygen, nitrogen, hydrogen, phosphorus, mercury, zinc, and sulfur were (correctly) identified as elements but also light and "<u>caloric</u>" (heat stuff), which he incorrectly believed to be a material substance. In 1775 he also recognized soot as being the element carbon, and more importantly, established that diamond was also carbon by doing the amazing experiment described below.

While Lavoisier's work was daring and pioneering, we need to be aware that Lavoisier could not really prove beyond any doubt if some substance was an element or a compound. His inclusion of carbon, while correct, could also be seen as a lucky guess. It was not clear, for example, which manifestations of the element were really carbon. Some experiment by one Guyton de Morveau much later in 1799 lead others to believe that only diamond would be pure carbon, while graphite would be an oxide of the "1st degree", charcoal of the 2nd degree, and carbonic acid, finally, would be the "complete oxide". Pepys and Allen corrected that in 1807, which helped Dalton in formulating his "law of multiple proportions" in 1808, paving the road to atoms and the periodic table. Of course, Lavoisier was neither alone in his enterprise nor did everybody believe him right away (or later, considering that there are mistakes; see below). The eminent *Priestley* , for example, also credited with "discovering" oxygen, never believed him at all.

It goes wothout saying that the people actually making and working with iron and steel couldn't have cared less for quite a while. Major insights were fine around then but usually not all that helpful for practitioners.



Some time in 1772, Lavoisiser and some of his buddies pooled their funds, purchased a diamond, put it into a closed glass jar, and focussed the rays of the sun on it with a big lens, supplying the ultimate "clean" heat. The **diamond** disappeared and since the weight of the glass jar was unchanged, the unavoidable conclusion was that the diamond had turned into a gas that could only be carbon dioxide, proving that a diamond was pure carbon. The experiment was not as simple it as it appears nowadays, as this contemporary illustration proves:



I don't know how Lavoisier's insight was received by the public but will bet that almost nobody believed him (and that his wife was mad at him for destroying that diamond). The judge who had him beheaded in 1794 said: "*La République n'a pas besoin de savants ni de chimistes ; le cours de la justice ne peut être suspendu*" (The Republic needs neither scientists nor chemists; the course of justice cannot be delayed). Well, Lavoisier also supported the <u>metric system</u>, and fought for the rights of a number of foreign-born scientists, including mathematician *Joseph Louis Lagrange*, during the Reign of Terror, so he had it coming for himself.

In essence, the 18th century was when "chemistry" was born. This was a difficult delivery because it required not only to do away with the "four element theory" (plus "aether" or "quintessence", added by Aristotle, being <u>wrong as</u> <u>ususal</u>, as the fifth element) but also to get rid of the more modern "<u>phlogiston</u>" theory. Boyle and Lavoisier, mentioned above, were decisive in this enterprise, but also a lot of other fledgling scientists.

Carl Wilhelm Scheele noticed in 1799, four year after Lavosisier recognized soot to be carbon, that graphite was carbon, too. Scheele also *proved* (as far as was possible) the elemental character of: Barium (Ba), Chlorine (Cl), Fluorine (F), Manganese (Mn), Molybdenum (Mo), Phosphorous (P), Oxygen (O)

Of course now you wonder. Just above I wrote that Lavoisier had oxygen, nitrogen and so on listed as elements and that was earlier. Well, as far as oxygen is concerned, I must also mention **Joseph Priestley** who described a special gas - we call it oxygen - in 1774, even before Lavosisier. I guess the discovery of oxygen and nitrogen was in the air, so to speak. As far as priorities go, Scheele probably made his discoveries in 1773, even before Priestley, but published it later than Lavoisier. Whatever, Priestley and Lavosier were English and French and thus not trustworthy; look what they did with Lavoisier. Scheele was German and now you could believe it. Scheele won ever-lasting fame by being instrumental in overturning the phlogiston theory.

Smithson Tennant, an English chemist, not only discovered the elements iridium (Ir) and osmium (Os) but proved in 1797 once more, but now also beyond reasonable doubt for the imbecile, lawyers and politicians, that diamond is indeed a phase of carbon. He did that together with his assistant William Hyde Wollaston, another well-known name in scientific circles, by reacting one part (= mol) of carbon with two parts of oxygen, obtaining nothing but carbon dioxide (CO<sub>2</sub>).

So at the beginning of the 19th century it was clear that soot, graphite, diamond, coal, coke and charcoal were just different manifestations of the element carbon, containing more or less "dirt" on the side.

In the following 150 years the understanding of carbon manifestations was refined and developed in great detail but nothing really new was added to the list above until about 1950 when (small) diamonds could be synthesized to some extent. Somewhat later, around 1970, the new and exciting carbon manifestations known under names like "Bucky balls", fullerenes, carbon nanotubes and graphene, started to appear, causing major scientific orgasms. The party is still on. This is described in another module.

Nitrogen (N), and Tungsten (W).

Illust. Link Carbon Phases

### It's Carbon That Makes Steel!

Everybody involved in the early iron and steel industry knew that the there were pronounced differences between (wrought) iron, steel and cast-iron and that one could change the properties of these materials to a large extent. One could even make steel from both wrough iron and cast-iron by some proper processing. Some of the practitioners of old must have given some thought to the question of what is responsible for the differences. Unfortunately, none of them wrote it down, or if somebody did, it was lost.

Most people thinking about that probably <u>followed Aristotle</u> and considered steel to be a more refined form of iron and thus were completely wrong. The question thus is: When did it become clear that steel is actually "dirty" iron, and that the most important dirt in this context was carbon? The answer is: In the 17th / 18th century - but details are a bit muddled. It can't be otherwise. You cannot possibly figure out that carbon is the decisive element for steel making if you lack both: a valid concept of elements and an idea of what is carbon.

We do know, however, that René Antoine Ferchault **Réaumur** (1683-1757) figured out that steel is "dirty" iron. He may not have been the first one to entertain this notion but he did clever experiments and wrote about it at length. It's the same Réaumur, by the way, to whom we owe the <u>Reaumur scale</u> for measuring temperatures. He is famous for a lot of other things but he seems to be the first (proto)scientist who conducted a systematic study into the production of steel. That wasn't just for fun. In the early 18th century the French iron and steel industry was seriously backward, and the French, intend on conquering the world even so they lacked <u>decent beer</u>, needed decent hardware for fighting and shooting.

Réaumur was able to obtain documentation concerning the iron and steel industries of foreign countries and his direct boss, Philippe II, duke of Orleans, subsidized Réaumur's research by granting him a pension of 12,000 livres (presumably a lot) to further his studies concerning iron and steel.

In Réaumur's times the basic product of the ferrous industry was "pig iron" (= cast-iron) from early blast furnaces, from which wrought iron was made. Steel was produced by "cementation", i.e. by mixing iron and charcoal and heating the mix for weeks, until the iron was carburized to what was called "blister steel". France somehow missed the advent of this new technology but Réaumur knew about it and thus didn't have to think too hard to get the idea that steel was iron *plus* something. It's however, not quite as obvious as it looks to us. Not knowing that wrought iron is rather pure iron, the cementation process could just as well have sucked something out of the wrought iron and thus turned it into steel.



Steel (!) engraving of Réaumur Réaumur went at it systematically and did what a true scientist would do: He charged lots of identical small crucibles with wrought iron plus all kinds of stuff that could supply the "cement" needed for making steel, and heated the mix under "rigidly" controlled conditions. Essentially he tried to change just one variable from experiment to experiment, exactly the right thing to do even in modern science.

After a large number of experiments Réaumur concluded that the best mixture for making steel out of iron was to use a specific combination of chimney soot, charcoal, ashes, and common salt.

More important, his general conclusion was that steel was in fact *impure* iron, somehow intermixed with "sulfurous and saline particles." More than that, he also concluded - correctly - that cast-iron was even more impure than steel.

But *sulfur*? Looks like he didn't recognize that the essential stuff needed to make steel was actually *carbon*? Well - carbon hadn't been "invented" yet, look above. In the early eighteenth century chemistry, "sulfurous" was the general term for inflammable stuff or for the "oily principles" contained in combustible substances, such as charcoal, soot, or whatever else could be lit up. It didn't just mean the *element* sulfur (S). Thus Réaumur was rather close to answering both essential questions from above in 1722, when he published his studies entitles "The art of converting wrought iron into steel" and "The art of making cast iron malleable" (of course the original titles were in Latin).

Réaumur actually did far more. He investigated the structure of fractured iron and steel pieces and tried to explain a lot of things from the differences he observed (iron - fibrous; steel - lamellar; cast-iron - granular; not too bad). Lacking a microscope and proper preparation methods, not to mention the concept of atoms, crystals, grains, and so on, he could not possibly arrive at the truth but got much closer than his contemporaries. For example, he maintained that quenching changed the structure of the metal without putting some "vital juices" from the water into the steel. He also put an end to the mythology about **quenching agents** (water, oil, blood,...) by pointing out that it is only their different ability to cool (we would call it different thermal conductivity) that was important. Most remarkable, perhaps, he reasoned that the infusion of his "sulfurous and saline particles" made not only hard steel out of soft iron, but also hard and brittle cast-iron depending on how much of the stuff was infused. That is essentially correct. Cast-iron was very important for making cannons but also very dangerous because you tended to kill about as much of your own soldiers by exploding cannons made from the brittle stuff as enemy soldiers by getting the cannon ball over there. Malleable cast-iron, that actually could be cast, (in contrast to steel), would have been of utmost importance - but didn't exist.

Réaumur figured that one could make malleable cast-iron by taking some of the "sulfurous and saline particles" out of the ubiquitous brittle cast iron. He thus could be seen as the grandfather of the first "designer" steel. He even found a method to do so but (cover the cast-iron with some hard-to-get mysterious substance then know as "saffron of Mars") but (wrongly) considered that not to be practical, due to the rarity of the stuff. Much later in the 19th century, the "Réaumur process" was actually used on a large commercial scale because the mysterious reddish stuff turned out to be simple iron oxide or iron ore.

The next guy who must be mentioned in this context, is **Torben Olof Bergman** (1735-1784), a Swedish subject. Sweden was a major producer of iron and steel and used to be a superpower that liked to invade Germany, Denmark, Finland, Russia, and so on, until it was reduced to roughly what it is today in 1721. Bergman, from Sweden's Uppsala University, published a book called "Dissertatio Chemica de Analysi Ferri" in 1781 (together with his Ph.D. student Gadolin; the book was essentially his thesis, it appears) in which he sought explanations for the different types of iron and steel in terms of the metal's chemical composition. He reasoned, not quite correctly, that only elements commonly found in the ore could be responsible for the changes in the metal: sulfur, plumbago, arsenic, zinc, and manganese. Note that "chemistry" in the modern sense was around the corner but that Lavoisier's seminal book was to appear 8 years later.



In contrast to Réaumur, who arrived at this conclusions by synthesis, by making steel, Bergmann's approach was analytical: look what is in there. That's why Bergmann is sometimes called the father of analytical chemistry.

Bergmann is sometime given credit for discovering that it is *carbon* that makes steel out of iron. To understand that we need to remember that "plumbago", while meaning lead (Pb) in principle, also was the name for graphite. In 1781 Bergman reported he had found that cast iron contained up to 3.3% of 'plumbago', steel contained up to 0.8% and wrought iron less than 0.2%. You can't do much better that that. One of Bergmann's student was <u>Carl Wilhelm Scheele</u> mentioned above and by now the proto-science of iron and steel was well on its way.

Finally, in 1786, **Gaspard Monge** (1746 -1818), **Charles Augustin Vandermonde** (1727–1762) **Claude Louis Berthollet** (1748-1822) published major work that finally used the word carbon (actually "charbone") instead of "plumbago" or "sulfurous particles" and thus put an end to the basic question of what makes steel.

Well - not quite. While it became clear to the initiated that you could make steel by putting some carbon in otherwise pure iron, you could make steel in the sense of "hard iron plus something" also by many other means, e.g. with <u>phosphorous</u>. And hardness was only one important property. Just as important (and rather unclear) were properties like malleability, "cold shortness" and "red shortness", and just as much or even more work was spend on the questions coming up in this context.

Since even the late 17th /early 18th century scientists knew more about that than we you do at this stage; I'll stop now. Rest assured that the matter will come up again further down this Hyperscript.