A natural advantage? Using mined graphite to make graphene

There are several ways of producing graphene out of everything from rocks to thin air. *Laura Syrett* looks at the benefits of using natural graphite, an industrial mineral with a modestly-sized market, as a source from which to make this game-changing material.

Since its discovery almost a decade ago, speculation about the revolutionary potential of graphene, the two-dimensional material consisting of a single layer of carbon atoms with phenomenal strength and conductive capacity, has flourished.

From flexible electronics and invisible aircraft to clean water and cancer treatments, there seems to be scarcely any area of modern life where adding graphene might not one day offer considerable improvement.

As a consequence, finding ways to produce the material in usable commercial quantities is being heavily funded in universities and corporate R&D departments around the world, while commercially-savvy scientists are moving quickly to protect the most promising fabrication methods with patents.

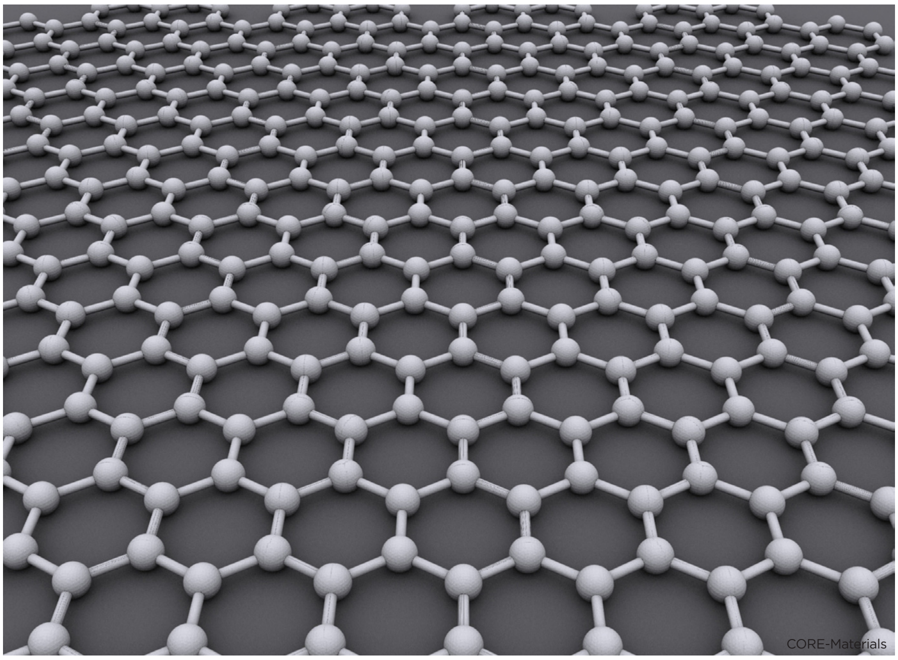
There are several routes to producing graphene, including growth from a solid carbon source using thermo-engineering, sonication, dissecting carbon nanotubes and carbon dioxide reduction.

One of the most cost-effective methods under investigation is the process of using natural graphite, a geologically abundant industrial mineral mainly used in the steel industry, as a 'parent material'.

Natural graphite can be used to produce graphene in a number of ways. The most common process trialled to date has been based on graphite oxide reduction, although variations on this method are beginning to emerge.

The discovery that natural graphite could be a real contender in the graphene supply chain has prompted many in the mining industry to follow the material's development with interest.

Many junior explorers are unsurprisingly eager to associate themselves and their projects with the hype, and even established miners such as Imerys-owned graphite producer, Timcal, have put their cards tentatively on the graphene table.



Discovered in 2004 by Professors Andre Geim and Konstantin Novosolov at the UK's University of Manchester, graphene is a single layer of carbon atoms that share the same hexagonal lattice structure as graphite.

However, some influential industry figures remain unconvinced that the super carbon will ever become a consequential market for mined graphite.

Naturally better?

Natural graphite is formed metaphorphically from organic carbon-containing substances and has a planar, layered structure, with each layer being made up of carbon atoms linked together in a hexagonal lattice. These links, or covalent bonds as they are more technically known, are separated by just 0.142 nanometres and are extremely strong.

As a derivative of graphite, graphene is composed of a single layer of these atoms and is so thin that it is almost invisible, and yet it retains the extreme strength imparted by the lattice structure. It also preserves other desirable properties of graphite, including the ability to effectively conduct electricity and a resistance to intense heat and chemical attacks.

Although synthetic graphite can be used to produce graphene, and has the benefit of consistency in terms of purity, natural graphite is significantly – up to ten times – cheaper than synthetic material.

This is because synthetic graphite is made by combining costly calcined petroleum coke with carbon black, and either anthracite or natural graphite, in addition to various binders and pitches, and is highly energy-intensive.

For graphene producers, cost considerations are important when it comes to making a material that can be economically scaled up for commercial adoption. Even more crucial, however, is the question of quality, an area where natural graphite also has an advantage.

Isolating graphene

According to chief scientist and co-founder of Canadian graphene developer Grafoid Inc., Gordon Chiu, there are a host of reasons why natural flake graphite is considered a preferred source for graphene versus synthetic graphite, carbon dioxide, natural gas or other carbon substances.

"We chose natural flake graphite as a starting material because only this source provides few-layered graphene without chemical modification," Chiu told **IM**.

Grafoid is working with TSX-listed explorer Focus Graphite to develop graphene using graphite ore from Focus' Lac Knife exploration project in Quebec. Both companies are also working with the National University of Singapore (NUS) spin-off, Graphite Zero Pte, to develop commercial graphene products.

"Natural graphite is made of many millions of layers of graphene stacked together. So, when we separate these layers, we get graphene," Chiu explains.

He notes that, since graphene's discovery, scientists working with natural graphite to produce graphene have used what is known as the Hummers method to turn graphene oxide into reduced graphene oxide (or rGO – a term which Chiu says has been incorrectly and interchangeably used with the term 'graphene').

The problem with this technique, Chiu says, is that the quality of graphene sheets produced is defective.

"The Hummers method to create rGO goes against the benefits of preserving the pristine nature of the material," Chiu explains.

"This chemical method involves pre-intercalation, intercalation, oxidation and other reduction chemistries. The Raman spectroscopy of the isolated material shows that the attempted scaling of Hummers has created uncontrolled imperfections to the material and heavy losses in investment dollars."

"The scaling of this reaction is also dangerous, the yield is low and recovery is a challenge," Chiu says, pointing out that, in terms of reproducibility, the quality control of each run of graphene made using the Hummers method throws up certain differences that may be unacceptable to commercial end-users.

Most graphene derived from natural graphite used for application development during the last ten years has, in some way, been crushed, pulverised, oxidised, reduced and leeched by strong acids, sacrificing quality to achieve scalability and thereby producing results below the theoretical potential of pristine graphene.

Physical methods of isolating graphene, such as mechanical exfoliation, or the so-called 'scotch tape' technique used by professors Andre Geim and Konstantin Novoselov in 2004 to first isolate graphene, are capable of producing high quality graphene, but are not scalable.


Graphenea

Billions of dollars are being ploughed into graphene research in university and commercial laboratories around the world.

Graphene intermediates

As the level of interest in graphene snowballs, improvements are being made to rectify the downsides of both physical and chemical techniques, and viable production methods using natural graphite as well as other source materials are beginning to emerge.

In May this year, Focus Graphite launched its first trademarked graphene product, MesoGraf, an intermediate material based on one-step method of exfoliating natural graphite ore.

"When we joined the NUS team with our raw ore process, in record time we managed to isolate a material that can be transformed more or less instantly into graphene," Chiu told **IM**.

According to Chiu, MesoGraf can be used for applications ranging from batteries and chemicals to energy storage, and Focus says it has already received product orders from companies in each of these business sectors.

Since then, Grafoid has also set up a JV company with the Quebec-based biomedical research firm ProScan RX Pharma Inc. to develop graphene-based treatments for cancer.

The new venture, called Calevia Inc., will work on using MesoGraf, to engineer targeted photothermal therapy that eradicates tumours while avoiding some of the side effects and limitations associated with existing cancer therapies.

The collaboration with ProScan is Grafoid's first foray into the medical industry, but Chiu says that there is significant potential to use natural graphite to develop a whole product portfolio of graphene-based sulphurs for use in the medical industry.

Graphene inks

In the UK, a country recently chided by its national media for seeming to fall behind in the global graphene race after fostering the material's discovery at the University of Manchester, a handful of firms including Wales-based, Haydale, have made impressive headway with marketable graphene technology.

Haydale, a wholly-owned subsidiary of Innovative Carbon Ltd (ICL), was established in 2003 as a spin-out from Swansea University to provide nanomaterials to the advanced materials community.

The company initially focused on purifying and functionalising carbon nanotubes, allowing them to be surface engineered for integration into host membranes or matrices.

This expertise in carbon nanomaterials was subsequently applied to converting specific and identified mined graphite ore into functionalised graphenes with the development of the 'Split Plasma' process, a versatile and scalable method of producing high quality graphene nanoplatelets.

Haydale says that its graphite comes from a sustainable provider with proven quality controls to ensure consistency of supply, although it has not publicly revealed its source.

Able to work at low temperatures, Haydale's natural graphite-based process is environmentally friendly and the trademarked HDPlas graphenes it produces have been supplied to over 100 leading research

Mechanical exfoliation or 'scotch tape' methods are capable of producing pristine graphene in small quantities but are not scalable.

institutions worldwide, and are finding commercial applications in inks, sensors, energy storage, photovoltaics, composites, paints and coatings.

"Haydale's process for functionalisation is significantly quicker and substantially more cost efficient than alternative methods of producing graphene nanoplatelets," the company told **IM**.

"Competing technologies such as the current 'wet' methods using acid-based processes as a cleaning and oxidising agent inevitably damages the nanostructures, degrading their integrity and mechanical strength," it explained.

"Critically it is often found that wet chemistry or thermal methods of producing graphenes do not fully remove the residual postproduction impurities such as catalyst metals."

Haydale entered into collaboration with local ink manufacturer Gwent Electronic Materials and in June 2013 and launched a graphene conductive ink without any metal additives.

According to the company, its HDPlas Graphene Ink Sc213 boasts a conductivity better than normal carbon based inks at a sheet resistivity of <10 ohms/sq.

Specifically formulated for screen-printing applications, the ink can be adapted to Flexographic and Gravure printing techniques. Haydale adds that the inks are fully customisable and can be modified with development partners for specific requirements including flexible displays, sensors and plastic electronics.

Another company with its sights set on the graphene inks market is the Canada-based graphite junior, Lomiko Metals. Lomiko is working with US-headquartered Graphene Laboratories to turn ore from its Quatre Milles deposit in Quebec into graphene materials.

"Because graphite has the same composition and arrangement as graphene, natural graphite is a popular and cost-effective precursor in the production of many graphene materials, including graphene nanoplatelets, reduced graphene oxide, and graphene oxide," Dr Elena Polakova, CEO of Graphene Laboratories told **IM**.

According to Polakova, the most important physical properties that a natural graphite source must have to make it suitable for graphene production are ultra-high purity and high crystallinity.

"Unlike graphite as a commodity, a larger flake size is not advantageous, and actually a smaller flake size is better," Polakova explains.

"When converting Lomiko's natural graphite to graphene oxide, we oxidised the graphite using a modified version of the Hummers Method; this method uses mostly non-hazardous chemicals in the oxidation process, so it is safe and commercially scalable," she said.

"In order to restore some of graphene's natural properties – because graphene oxide is not conductive like graphene – we reduced the samples to create reduced graphene oxide. We then went a step further and converted the reduced graphene oxide into a paste with applications in conductive inks and coatings."

Polakova says that while the company has initially focused on the inks market, graphene made using these methods could have a wide range of commercial applications.

"Currently, we are researching the graphene's potential in supercapacitors in conjunction with Stony Brook University's SensorCAT and Advanced Energy Research and Technology Center," she said.

"At the moment, we have the capacity to make kilograms of graphene using these processes, but it will be easy for us to scale up our processes when demand rises. Although there is a lot of hype surrounding graphene, we are very close to seeing its first true commercial applications," she added.

Graphene batteries

Norway, a historic natural graphite producer, is also looking to take advantage of its indigenous reserves of the mineral and world-leading research capabilities to establish a graphene science industry.

Abalonyx, a Norwegian technology start-up company, has been working with graphene and graphene derivatives since 2008.

"It is well known that certain natural graphites are excellent raw materials for producing graphene in the forms of graphene oxide, chemically converted graphene and reduced graphene oxide," Rune Wendelbo, founder and CEO of Abalonyx, told **IM**.

Like Graphene Laboratories, Abalonyx used a modified version of the Hummers method to develop a safe, scalable and reproducible process for making graphene from natural graphite, which has been automated and is now being commercialised.

Abalonyx has entered into a non-exclusive strategic agreement with Norwegian graphite junior Nordic Graphite to focus on developing a vertically integrated supply chain for graphene production, and the companies are presently working jointly to scale up Abalonyx's process to demonstration scale.

"We are also looking at other interesting materials such as vein graphite from Sri Lanka, and plan to start demo-production in 2014," Wendelbo said.

"For natural graphite to be the preferred raw material, it must be close to 100% crystalline, which is normally not the case with synthetic graphites," he explains.

"We ran a pilot reactor for two months in 2012 using purified natural graphite as raw material. The purpose of the pilot run was to confirm scalability, reproducibility and safety as well as acquiring a basis for our production cost estimates. Our cost estimate shows graphene oxide can be produced for €22 ($30*)/kg," he said.

Bags of potential: natural flake graphite could emerge as the raw material of choice for future graphene production.

"With our process, most impurities can be tolerated, up to a level of 5% or so, because they are separated from the graphene together with other wastes," Wendelbo notes.

"In terms of flake size, there is no rule, but larger flakes will require longer process time. For some end-uses, smaller flakes are preferred whereas for others, larger flakes are preferred."

"For example, our sister company, Graphene Batteries, uses our graphene for battery applications, which have special requirements for product properties in order to boost battery performance. Graphene Batteries optimises Abalonyx's graphene materials for their applications, as other end-users would do," he added.

Chinese graphene

While there has certainly been no shortage of graphene development in North America and Europe, efforts in these regions are being outstripped by Asia's determination to crack the commercial potential of graphene science.

A study released by the UK-based consultancy CambridgeIP earlier this year into the number of graphene patents worldwide found that China is leading the pack by a significant margin, with 2,204 patents filed as of 1 February 2013, compared to 1,754 in the US and 1,160 in South Korea – the two closest followers.

"One of the striking features of the [IP] landscape is the marked increase in graphene patent activity in Asia, especially South Korea and China, over the past several years," said Quentin Tannock, CambridgeIP Chairman, when the research was published.

As with elsewhere in the world, the spectrum of graphene research being conducted in China and South Korea is vast, but here, too, natural graphite-based processes account for a significant proportion of the total number of projects currently underway.

"We are making graphene out of natural graphite without any other source," Johnson Fung, CEO of the eastern China-based graphene company, Xiamen KNnano, told **IM**.

"The process techniques we use include physical and chemical methods, but the physical method is preferred," he said, adding: "we think that this method is the right way to make the graphene under volume production."

Although Fung is optimistic about the near-term potential of natural graphite as a graphene raw material, he remains open-minded about whether the mineral will emerge to be the industry's precursor of choice.

"We are not sure. Graphene is so young as a new kind of material and there are so many things should to be done in the graphene field," he said.

He also thinks that China has the potential to become a world leader in commercial graphene development. "Some Chinese companies have the capability to produce more than 300 tonnes of graphene material per year. Some industrial application will come at some stage," he predicts.

Jiang Xu, a developer at the Nanjing University spin-off, XianFeng Nano Material Technology Co. (XF Nano), said that his company is also actively investigating natural graphite's graphene-source potential, and has already produced some promising results.

"We can achieve graphene of good quality from natural graphite," Jiang told **IM**, "but we are looking at other source materials as well".

XF Nano is working with undisclosed laboratories in the US, Singapore and China, and is already exporting its nano materials to countries around the world including the US, UK and Sweden.

"We think that Chinese firms will be able to manufacture and sell graphene at a competitive price," Rosalind Chen of Guangzhou-based Hongwu Nanometer told **IM**.

"We are already manufacturing and exporting graphene products for commercial applications including graphene polymer composites, high strength and conductive films, solar cells, electrochemical energy storage and catalysts," she added.

From lab to fab?

While there is no denying that much of the present hype surrounding graphene will fail to translate into commercial realities, for now it seems that the majority of the natural graphite industry is happy to ride on the material's publicity wave.

A recent poll of **IM** readers found that 57% of respondents believe that the graphene frenzy could help boost the graphite mining industry's profile if the nano carbon successfully achieves commercial traction.

However, 34% of respondents said that graphene would not provide natural graphite producers with any tangible benefits, and a further 10% felt that it was impossible to say at this stage in graphene's development.

One of the main objections raised by those who doubt graphene's importance as future consumer of natural graphite is the fact that the industry is likely to be an extremely small-volume market.

Worldwide natural graphite demand presently sits at around 1m tpa, more than 80% of which is consumed by industrial applications, and it seems unlikely that graphene will make much of an impact on this figure, even if its full potential is realised.

According to Stephen Riddle, CEO of US-based Asbury Carbons, the future is for natural graphite in the graphene industry is distant, but by no means dark.

"The good news is that using natural graphite is less costly to produce graphene than other sources," he told **IM**.

"The bad news is that the type of products that can someday use natural graphite-based graphene are much more price sensitive, and will therefore take a lot longer to develop. And when I say a lot longer, I mean a lot longer," he added.

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