Unveiling Brazil's Potential in Graphene Nanotechnology: The Role of High-Quality Flake Graphite

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Abstract. This paper explores Brazil's significant potential in the field of nanomaterials and nanotechnology through the lens of high-quality flake graphite extraction for graphene production. With a focus on the geological advantages that render flake graphite prevalent in Brazil, particularly in regions like Minas Gerais and Bahia, we delve into the processes leading to its formation and the reasons behind its suitability for graphene manufacturing. The study emphasizes Brazil's strategic position due to its abundant reserves and the quality of flake graphite, which is paramount for the burgeoning graphene industry. It further investigates the industrial capabilities and infrastructure that bolster Brazil's role as a pivotal player in the global nanotechnology arena, highlighting the country's potential to influence the development of green technologies and advanced materials. Through comprehensive analysis, this paper showcases Brazil's untapped opportunities and challenges in leveraging its natural resources for technological advancement and industrial competitiveness in the global market for nanomaterials.

Keywords. Graphene, Brazil, flake graphite, nanotechnology, Araçuaí Orogen, São Francisco Craton.

1. Introduction

The advent of graphene, a single layer of graphite [1], has revolutionized the field of nanomaterials due to its exceptional physical and chemical properties such as high electrical conductivity of up to 80 MS/m [2], a uniaxial breaking strength of about 0.142 Nm per long carbon bond (being the strongest material ever discovered) [3], and excellent thermal conductivity in the range of approximately $(4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$ W/mK [4].

Graphene synthesis from graphite employs methods like Liquid Phase Exfoliation (LPE) and Chemical Vapor Deposition (CVD), each with distinct carbon source prerequisites. LPE necessitates high-quality flake graphite to facilitate efficient exfoliation and ensure superior graphene properties [5]. In contrast, CVD, a process involving the thermal decomposition of carbon-containing gases on a metal catalyst, does not require graphite, utilizing gaseous precursors for graphene formation [6].

The significance of graphite's layered structure, a result of carbon-rich materials metamorphism under intense heat and pressure, becomes evident in its role in graphene production, particularly for LPE. Regions like Minas Gerais and Bahia in Brazil, with their abundant and high-quality graphite deposits, highlight the country's strategic position in the nanotechnology and graphene sectors.

Brazil's geological formations are particularly conducive to the occurrence of flake graphite [7]. The country's unique tectonic history and extensive metamorphic regions, especially within Minas Gerais and Bahia, have resulted in the abundant presence of this mineral. These geological characteristics, coupled with Brazil's existing mining infrastructure and technological capabilities, lay the groundwork for the nation to leverage its natural resources more effectively.

Brazil's potential in the graphite extraction sector goes beyond its geological advantages. The strategic importance of graphite, especially in the context of nanotechnology, cannot be overstated. With global change and growing demand for high-tech materials, Brazil's ability to supply high-quality graphite for graphene production places it at a crucial juncture. This positions the country not only as a key player in the graphite market but also as a critical contributor to global advancements in nanotechnologies. Brazil has internationally renowned researchers, such as Professor Marcos Assunção Pimenta, thanks to such researchers, Brazil excels in innovations in the field of nanotechnology. However, the country currently faces challenges in the area of human resources, which will be discussed later in the article.

2. Research Metods

The research methods for investigating Brazil's role in graphene nanotechnology and the significance of high-quality flake graphite involved a systematic literature review and professional interviews. The literature review focused on collecting and analyzing existing studies, reports, and articles related to graphene, its applications, and the importance of flake graphite as a precursor material. Interviews were conducted with experts in graphene research, development, and application to gain insights into practical aspects, challenges, and the technological landscape in Brazil. An essential component of the research was the analysis of data from the "Informe de Recursos Minerais, Projeto Avaliação do Potencial da Grafita no Brasil - Fase 1" by the Serviço Geológico do Brasil – CPRM.

3. Graphite and Graphene

3.1 The Geological Pathways to Graphite Formation

The formation process of graphite is intrinsically linked to two primary geological mechanisms: contact or regional metamorphism of carbonaceous material, and deposition from carbon-bearing fluids or, less frequently, melts [8]. These processes yield distinct types of graphite: amorphous, flake, and lump, each categorized based on the metamorphic grade of the host rock or the method of deposition. Flake graphite, for instance, is typically associated with high-grade metamorphic rocks such as gneisses, quartzites, or granulites, indicative of the intense conditions required for its formation.

The geological settings conducive to vein graphite deposits, characterized by high purity and crystallinity, necessitate specific temperature and pressure conditions. These deposits are often found within high-grade metamorphic rocks (primarily granulites) and various igneous rocks, both plutonic and volcanic. The metamorphic conditions facilitating graphite formation, particularly in granulite facies terranes, involve temperatures and pressures reaching up to approximately 1,100 °C and 12 kbar, respectively [9]. These conditions underscore the extreme environment necessary for transforming carbonaceous material into graphite, marking a significant phase in the carbon cycle within the Earth's crust.

The distinct mineralogical and textural characteristics of vein graphite within these deposits play a pivotal role in determining its industrial applicability and value. The fine-grained rosettes or spherulitic aggregates, alongside coarser flakes or needles oriented perpendicular to vein walls, suggest varied conditions of graphite deposition and cooling rates [8]. These textural variations, often leading to zoning patterns across veins, are indicative of successive fracture openings and the dynamic nature of the graphite-forming process. Understanding these characteristics not only aids in identifying potential industrial uses but also in refining exploration strategies for high-quality graphite deposits, crucial for advancing current technologies and developing new applications.

3.2 Flake Graphite

The transition to flake graphite represents a remarkable natural process, influenced by specific conditions such as pressure, temperature, and the geological context. This form of graphite is distinguished from others by its unique crystalline structure and the specific conditions under which it forms, offering distinct advantages for a variety of industrial applications, including high-temperature lubricants, fluxes, high-quality refractories, metallurgy, coating, fuel cells, and batteries, and especially in graphene production.

The formation of flake graphite occurs as a result of additional crystallization of crystalline tar [10]. In the described process, further crystallization of crystalline tar in semi-graphite samples contributes to the development of flake graphite. This formation coincides with crystalline aggregates within the fractures of the matrix graphite. These crystalline aggregates fill the void cavities within the semi-graphite, while flake graphite distributes itself along the fractures of the matrix graphite alongside crystalline aggregates, arising directly from the crystallization of crystalline tar. This transformation implies that flake graphite possesses a less ordered structure compared to other forms of graphite but is characterized by its larger grain size, which may impact its properties and applications.

The purity of flake graphite is an essential consideration for the industry (fig. 1). High-purity flake graphite is crucial for achieving optimal performance in various applications, particularly those requiring materials with excellent electrical conductivity, thermal resistance, and mechanical strength [11]. The purity level directly affects the efficiency and quality of end products, making it a critical parameter in the selection of flake graphite for manufacturing processes.

Flake graphite is particularly suited for graphene production. Its layered structure allows for the mechanical or chemical exfoliation needed to produce graphene, a material composed of a single layer of carbon atoms. The ease with which these layers can be separated, thanks to the weak van der Waals forces holding them together [12], makes flake graphite an ideal starting material for producing high-quality graphene.

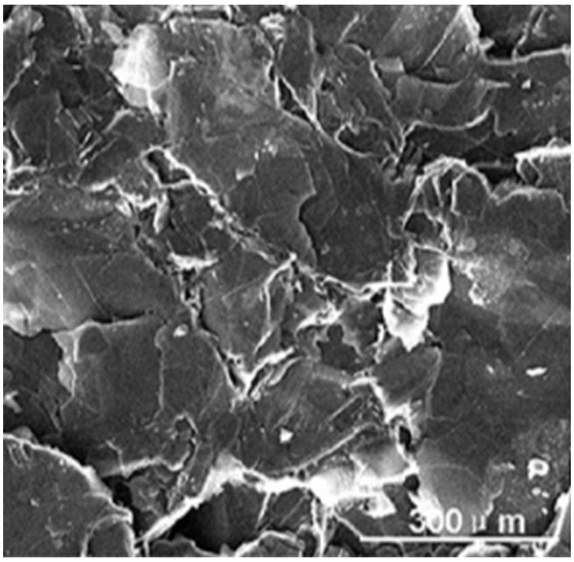

Fig. 1 – SEM images of the composites pristine graphite (Zhao Y. et al 2013).

3.3 Graphene

Graphene has emerged as a revolutionary material in the realm of science and technology [13]. Its discovery has led to a profound understanding of its remarkable mechanical, electrical, and thermal properties, positioning it as a material with potential to redefine current technological limits. Graphene's unparalleled strength, combined with its flexibility and lightness, makes it an ideal candidate for a new generation of composites and materials that are stronger yet lighter than any existing alternatives.

Electronically, graphene is a standout performer, with high electrical conductivity and exceptional charge carrier mobility, allowing electrons to travel with minimal resistance [13]. This property is critical for the development of advanced electronic devices, potentially leading to faster, more efficient circuits and components. Additionally, graphene's thermal conductivity is among the highest of any known material, making it an excellent medium for thermal management applications in electronics and other fields.

The impermeability of graphene to gases [14], despite its one-atom thickness, suggests promising applications in filtration and barrier technologies. Such a feature could lead to breakthroughs in air and water purification systems, as well as creating new types of protective coatings. Furthermore, the versatility of graphene extends to its chemical properties, allowing for functionalization and adaptation for specific uses, ranging from biomedical applications to energy storage solutions.

Despite its impressive array of properties, the commercialization of graphene-based technologies faces challenges, primarily in scalable and cost-effective production. However, ongoing research and development are dedicated to overcoming these obstacles, promising to unlock graphene's full potential in the near future. The continuous exploration of graphene’s properties and applications holds the promise of spawning a new era of technological innovations, impacting a wide array of industries from electronics to energy storage, and beyond.

4. Brazil Geology

4.1 Araçuaí Orogen

The Araçuaí Orogen (fig. 2), located in the southeast of Brazil, is one of the most significant structural components in the region's geology, extending from the southeast of the São Francisco Craton to the Atlantic coast, between the 15º and 21º S parallels. Formed during the Neoproterozoic-Cambrian period, this orogen's origin is related to the opening of the Atlantic Ocean in the Cretaceous, leaving two-thirds of its extension in Brazil. Its development is linked to complex tectonic events that include continental rifting, passive margin formation, and a series of orogenic phases culminating in continental collision [15].

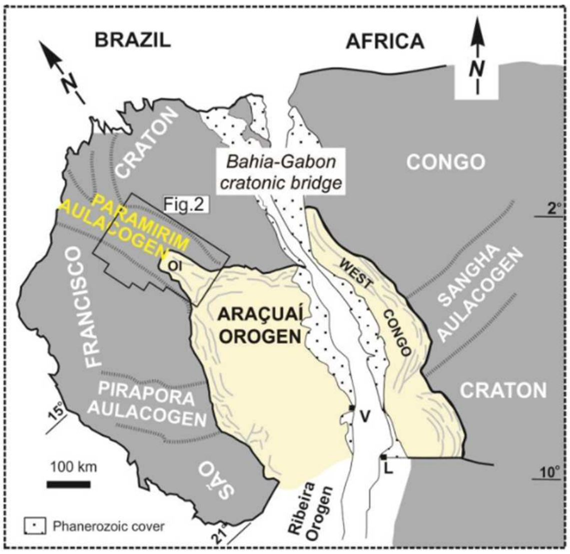

Fig. 2 - The Araçuaí Orogen in the central region of the Gondwana Paleocontinent (modified by Alkmim et al. 2006). FA, structural traces of the Araçuaí Fold Belt (sensu Almeida 1977); ZI, interference zone of the Araçuaí Orogen with the Paramirim Aulacogen.

In the Minas Gerais and Bahia region, the Araçuaí Orogen reveals a complex tectonic and lithological interaction. The presence of graphite, especially in the Jequitinhonha Complex and associated formations, is notable and constitutes an important mineral resource. These graphitic rocks indicate high degrees of metamorphism and are associated with the tectonic and metamorphic evolution of the region.

The Jequitinhonha Complex, located in the Araçuaí Orogen, is a geological entity of great importance in the region, extending through eastern Minas Gerais and southern Bahia. This complex is characterized by its lithological diversity, with a predominance of aluminous to peraluminous paragneisses, interspersed with quartzite, graphitic gneiss, and calc-silicate rocks.

The importance of the Jequitinhonha Complex transcends the structural aspect, being notable for the presence of one of the largest lamellar graphite deposits in Brazil, indicative of high-grade metamorphic conditions. Graphite, a pure carbon mineral, forms under high temperature and pressure conditions, suggesting that the complex underwent intense metamorphic processes that favoured the crystallization of this mineral.

4.2 São Francisco Craton

The São Francisco Craton (fig. 2), one of Brazil's fundamental geological structures, represents a significant piece of the Earth's ancient crust, encompassing a vast area that offers a window into the planet's early geological history. This craton is renowned for its extensive Precambrian rocks, which are over 600 million years old, making it a key area for studying the processes and conditions of the early Earth. Its stability over geological timescales has allowed for the preservation of a wide range of mineral deposits, including gold, diamonds, and, notably, graphite, making it a focal point for both academic research and mining activities [16].

The São Francisco Craton has undergone minimal deformation since the Precambrian, allowing it to retain a record of some of the earliest orogenic (mountain-building) events, metamorphic processes, and magmatic activities. The craton is divided into several blocks and terranes, each with its unique geological history and characteristics, bordered by mobile belts that record the collision and assembly of these ancient landmasses. This complex geological framework provides insights into the crustal evolution, including the formation of the continents and the atmosphere's early composition.

In the state of Bahia and the northern region of Minas Gerais, the São Francisco Craton showcases its geological diversity through distinct mineralogical formations and structures. This area is particularly noted for hosting some of Brazil's most significant gold and graphite deposits. The graphite deposits, often associated with high-grade metamorphic rocks, are of great industrial importance due to their high quality and purity.

4.3 Graphite Formation at the Boundary and Adjacent Areas of the São Francisco Craton and Araçuaí Orogen

The geological events leading to graphite formation within the São Francisco Craton are a result of a confluence of metamorphic, tectonic, and hydrothermal processes, each playing a vital role in transforming organic matter into graphite [17].

Initially, the deposition of carbon-rich organic material in sedimentary basins, followed by its subsequent burial into the Earth's crust through tectonic processes, sets the stage for graphite formation. Subjected to high-pressure and temperature conditions during episodes of regional metamorphism, this organic material begins to transform. Regional metamorphism, characteristic of orogenies and continental collisions, acts as a primary driver for graphite crystallization, with amphibolite to granulite facies conditions being particularly conducive.

During these metamorphic events, temperature and pressure reach levels that not only trigger the structural and chemical reorganization of carbon but also facilitate the mobilization of carbon-rich fluids through the crystalline basement. These fluids, traveling through faults and fractures in the São Francisco Craton, precipitate graphite in veins or lenses upon encountering favourable conditions, such as a decrease in temperature or interactions with host rocks. The association of pegmatites and quartz veins with graphite deposits suggests that graphite crystallization occurred synchronously with the solidification of these magmatic intrusions, marking a close temporal relationship between high-temperature metamorphism, hydrothermal activity, and graphite formation.

4.4 Graphite Crystallization in Brazil

In Brazil, graphite occurs across a wide spectrum of temperature and pressure conditions, ranging from low-grade green schist facies to high-grade metamorphism in the granulite and eclogite facies, often undergoing thermal alteration through contact metamorphism. Generally, mineralization's are concentrated in three metamorphic facies: green schist (27.2%), amphibolite (24.8%), and amphibolite-granulite (23.1%). When the variations within the amphibolite facies (from high to low) are aggregated, they account for 50.4% of the occurrences, while the green schist facies (from high to low) represents 38.7% of the total. This suggests that the amphibolite facies have the greatest potential for hosting graphite mineralization's, followed by the green schist facies. The granulite (5.4%) and hornfels (5.5%) facies have almost identical proportions, demonstrating a lower potential for graphite mineralization's [18].

From a metallogenetic perspective, the amphibolite facies are indicative of flake and/or vein graphite with higher degrees of crystallinity and purity. Conversely, the green schist facies suggest a correlation with amorphous to flake graphite with a lower degree of crystallinity. Finally, the metamorphic conditions most favourable for finding vein and/or flake graphite are granulite and hornfels, although epigenetic mineralization's may be associated with granitic intrusions or anatexis.

The flake-type deposits in Brazil range from 0.72 tonnes to 100 Mton ± 17 Mton. The deposits form stratabound, tabular, and lenticular bodies, with grades ranging from 3 to 65 %Cg [18]. Here, the grades are a direct function of the regional metamorphic degree the protoliths have undergone (fig. 3).

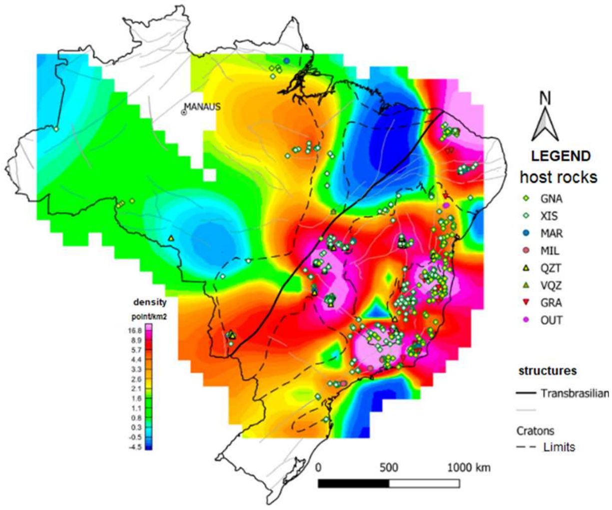

Fig. 3 - Map of the density distribution of points (points/km^2) of Brazilian graphite mineral resources registered by SGB/CPRM. GNA: Gneiss, XIS: Schists, MAR: Marble, MIL: Mylonite, QTZ: Quartzite, VQZ: Quartz Vein, GRA: Granites and granitoids, OUT: Lithotypes related to contact metamorphism. Thick black line: megastructure (Transbrasiliano Lineament); gray lines: main deformation zones; Dashed lines: Cratonic boundaries.

5. Research and Industry in Brazil

5.1 Extraction Techniques and Global Market Influence

The morphology of the terrain, the deposit, and the depth of the ore body are essential factors determining the mining method used [19]. Graphite can be extracted through open-pit or underground mining (stoping and filling), particularly for vein and amorphous graphite types [20]. Underground mining for flake graphite is advised only for layers with a graphite content over 15% Cg [18].

Graphite is chemically inert and considered a resistate mineral. The development of a lateritic profile in graphite deposits is a distinctive feature of those located in tropical regions like Brazil. This trait eases manual excavation using shovels and pickaxes, rather than mechanical processes involving tractors. In some cases, mild blasting is necessary to prevent fragmenting the ore and altering the graphite's crystalline structure.

Brazil's status as the world's fourth largest graphite producer (United States Geological Survey and World Mining Data 2022) is indicative of its notable presence in the global market. In the first half of 2023, Brazil reported significant revenue and production figures in the graphite sector, achieving a revenue of USD 38.75 million and a production volume of 457,000 tonnes in the first half of 2023, the country has shown its ability to generate significant output within this sector, as documented by the National Mining Agency (ANM) and the Brazilian Mining Institute (IBRAM).

Holding approximately 28.8% of the world's graphite reserves (ANM, 2017), Brazil is a key player in the supply of this mineral. The prominence of companies like Nacional Grafite Ltda. in this sector exemplifies the dynamism and power of Brazil's graphite industry, along with its pronounced influence on the international market scenario. Nacional de Grafite Ltda., the leading graphite mining firm in Brazil, accounts for 84% of the country's graphite output. This company is situated in Minas Gerais, specifically in the towns of Itapecerica, Pedra Azul, and Salto da Divisa.

5.2 Research and Perspectives

To produce graphene economically, the LPE method is used, which extracts graphene from abundant and cheap graphite, ideal for less critical applications such as composite materials and conductive paints due to its simplicity and low cost [5]. However, high-tech applications require high-quality graphene, obtained through the more complex and expensive CVD method, which generates continuous and pure layers of graphene, necessary for advanced electronic devices. Brazil, with its notable history in graphene research and significant advancements, has the potential to be a powerhouse in the graphene sector [6]. The country's research has benefited from the low initial cost of producing graphene, largely due to the LPE process, coupled with the availability of flake graphite and the establishment of research networks, which have reinforced scientific development.

The CTNano (Nanomaterials and Graphene Technology Center), a specialized technology center, demonstrates Brazil's capability to bridge academic research and industrial needs, converting scientific knowledge into technological innovations. However, the major obstacle facing Brazil's ascension in the graphene field is not just financial constraints but also the shortage of human resources. The need for robust and continuous funding in science and technology, prevalent in earlier decades, has waned, with recent investment reductions hindering Brazil's ability to sustain its proactive and innovative role in global graphene research.

In interview, professor Marcos Assunção Pimenta, one of the creators and the general coordinator of the CTNano, and currently the coordinator of the National Institute of Science and Technology (INCT) of Carbon Nanomaterials, Brazil's qualified human resources and their substantial contributions to graphene science globally are noteworthy. Yet, to truly harness the nation's potential and become a leading force in the graphene industry, Brazil must overcome the current challenge of cultivating and retaining skilled professionals in the field.

In this way, in Brazil, neoliberal political reforms and consecutive funding blocks have exacerbated difficulties in the scientific sector over the last decade. These challenges have created a particularly adverse environment for researchers at state universities, severely limiting the capacity for knowledge production. An analysis of post-2018 election economic policies reveals how the dominance of financial capital has transformed science into technoscience, where profitability is often prioritized at the expense of sustainable and progressive scientific advancement [21]. Additionally, data indicate a sharp decrease in public funding for science and research, marking the transition to an economic model dominated by financial interests that began in the 1990s [21]. These conditions have significantly reconfigured the role of state universities and the function of researchers in the Brazilian context.

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