Universal Journal of Carbon Research
https://ojs.wiserpub.com/index.php/UJCR/

Short Communication

Status quo of graphene geology in Brazil: mineralogical, petrological and materials science contributions

Valéria Stochero[1], Augusto Nobre[2*]

[1]Center for Technology, Federal University of Santa Maria, Santa Maria 97105-900, RS, Brazil
[2]Center for Natural and Exact Sciences, Federal University of Santa Maria, Santa Maria 97105-900, RS, Brazil
E-mail: augusto.nobre@ufsm.br

Received: 1 January 2024; **Revised:** 13 May 2024; **Accepted:** 13 May 2024

Abstract: This study investigates the current status of graphene geology in Brazil, highlighting its mineralogical, petrological, and materials science contributions. Three approaches are presented: (I) the natural production of graphene from graphite nanoplates in sheared rocks, (II) the geological simulation under laboratory conditions, and (III) the evolution of electrical resistance in geological formations containing graphite and talc. All reviewed studies underscore the efficacy of graphene production in particular geological contexts, demonstrating its efficient formation within shear zones. The results indicate that graphene stabilises in talc and exhibits improvement in electrical conductivity under specific thermodynamic geological conditions, suggesting abundant natural sources that are economically viable and possess industrial applications. A comparative analysis shows that, although natural graphite nanoplates are thicker than graphene, they still qualify as nanomaterials and demonstrate promising technological potential. The research contributes to understanding the natural formation of graphene and highlights its practical applications in the Fourth and Fifth Industrial Revolution.

***Keywords*:** natural graphene; graphite nanoplatelets; nanomaterials; mineral nanotechnology

1. Introduction

Graphene, a two-dimensional structure composed of a single layer of carbon atoms arranged in a hexagonal configuration, has garnered considerable interest in both the scientific community and industry, thanks to its remarkable properties (Nobre et al., 2021). The discovery of graphene through the technique of mechanical exfoliation and the subsequent revelation of its properties earned the Nobel Prize in Physics in 2010 for its discoverers (Geim & Novoselov, 2009). Since then, there has been a significant focus on synthesis methods and large-scale production of graphene, driven by its relevance in sectors such as electronics, energy, medicine, and advanced materials (Walimbe and Chaudhari, 2019; Catania et al., 2021; Kausar et al., 2023).

The increasing prominence and demand for graphene in the last decade are closely linked to the Fourth and Fifth Industrial Revolutions, effectively meeting the technological demands of this era of digital transformation. This technological revolution is characterised by the advanced integration of digital, physical, and biological technologies into industrial processes, promoting unprecedented interconnection between systems and driving intelligent automation (Groumpos, 2021; Ali et al., 2022; Noble et al., 2022; Zizic et al., 2022). With notable electrical conductivity at room temperature, as well as high hardness and flexibility, graphene emerges as a relevant raw material for devices in this high-tech context. Contemporary industrial evolution relies on highly efficient materials and the application of nanotechnology. Leveraging the unique characteristics of graphene for

DOI: https://doi.org/10.37256/2120244186

the fast transmission of digital data contributes to the effective generation, storage, and transportation of energy (Nobre et al., 2022a).

Despite the significant potential for this material, several challenges have not yet been completely resolved, particularly in large-scale production and in the stabilisation of graphene. The adhesion of graphene to a substrate, its dispersion in a solution, or its oxidation to graphene oxide (eventually succeeded by the reduction process), aiming to reduce surface energy, contributes to its high manufacturing costs associated with low productivity processes (Rodrigues et al., 2017; Ba et al., 2020; Nobre et al., 2022a). In this challenging context, it is important to note that a promising alternative to meet the demand broadly and economically may be represented by natural graphenes.

These natural graphenes are graphene-like structures that occur naturally in geological contexts, such as graphite-bearing metamorphic rocks in which the graphite has been exposed to a shear tectonic process until it reaches a thickness of less than 100 nm (Nobre et al., 2022b). Since these materials are naturally occurring and stabilized within rock formations, they provide affordable and abundant options for producing graphene-like substances. Despite the advantages in terms of availability and cost, it is crucial to observe that natural graphenes inherently present crystalline defects and impurities due to natural material manipulation processes. These imperfections introduce irregularities in the material's structure, affecting its properties (Nobre et al., 2022a).

Within this panorama, this study is based on a literature review that examines the studies that are being developed on graphene geology in Brazil, emphasising prospecting, experimental mineralogy and petrology and identification of these natural structures in rock samples.

2. Literature review

2.1 *World's first graphene geology initiatives*

Geology of graphene operates in two main research lines: the production of graphene from mineral raw material that has undergone simple beneficiation processes and the extraction of graphene and analogous materials (such as graphite nanoplatelets) directly from rocks (Nobre et al., 2022a). Studies in the area began in 2011, when the relevance of the crystallographic, physical, and chemical characteristics of graphite ore in the properties of graphene obtained from it was first raised in the literature (Ruiz-Hitzky et al., 2011). From Ruiz-Hitzky et al. (2011), the scenario was set that there is a need to characterise graphite mineralogical and petrologically to optimise the production of graphene that is produced from natural raw material. The geographic location and implications in graphite occurrence in the evaluation of electrical and electrochemical properties of graphenes were studied by Wong et al. (2015). Since silicates are common substances in rocks, they consequently become common contaminants in graphite, which was evaluated by Peng et al. (2016).

2.2 *Graphene geology in Brazil*

In Brazil, studies in this area of knowledge began in 2020, when graphite nanoplatelets were identified in mylonitic metadolomites of the Itaiacoca Group, in Paraná state. The work concluded that several factors acted together to make the material available, such as the mineral assembly predominantly constituted by platy minerals, shear efforts, and suitable pressure and temperature conditions (Nobre et al., 2020). From the discovery of graphite nanoplatelets stabilised in rock, laboratory studies were conducted to understand the process of obtaining graphite nanoplatelets and whether it would be possible to stabilise graphene in rock. Nobre et al. (2022b) confirmed this possibility from experiments conducted using the piston-cylinder apparatus in a mineral assembly formed by graphite and talc. In this experiment, there was systematic cleavage of the van der Waals forces of both minerals, with the exfoliated talc acting as a substrate for the graphene flakes formed.

Understanding that it is possible for graphene to form and stabilise in a geological environment, its electrical properties were investigated by Nobre et al. (2023). Various metamorphic conditions were evaluated in a mineral assembly composed of talc and graphite, which had demonstrably allowed graphene formation, to verify which conditions would form nanometric heterostructures with lower electrical resistance. It was determined that pressures exceeding 600 MPa cause severe deformation in the formed heterostructures, preventing the flakes from becoming interconnected. The electrical resistance when the flakes are connected causes the electrical resistance to drop substantially, indicating a way to identify and prospect these heterostructures in fieldwork.

3. Analytical procedures

In this section, we outline the experimental procedures employed in three studies discussed in the previous section (Nobre et al., 2020; Nobre et al., 2022b; Nobre et al., 2023). In Nobre et al. (2020), rock samples with mylonitic foliation were carefully chosen. The selected cuts allowed for a detailed observation of the mineral arrangement in this foliation using polarised light optical microscopy (petrography).

In the optical microscope, the graphite lenses most susceptible to shearing were identified and subsequently subjected to material extraction using a tungsten tip for Raman spectroscopy analysis. Nobre et al. (2020) addresses the inherent difficulties associated with the natural production of graphene, proposing the consideration of a viable alternative: natural graphite nanoplates. These nanoplates, by showing significant potential as substitutes for graphene, stand out as two-dimensional nanoscale materials. In the microscopic analysis using polarised light of sheared metadolomites from the Itaiacoca Group, a mineralogy composed of quartz, carbonates (calcite/dolomite), talc, graphite, and amorphous carbon allotropes was identified. The mineral grain size in the rock does not exceed 100 µm. The mylonitic foliation in these rocks is pervasive, generating compositional banding with graphite-rich bands intercalated with bands consisting of quartz, carbonates, and talc. The sheared metadolomites rich in graphite were documented through micrographs, highlighting the intercalation of graphite-enriched bands between zones of dispersed graphite in the matrix.

In Nobre et al. (2022b), the simulation of geological graphene genesis is conducted, providing a deeper understanding of how graphene can naturally form in low-grade metamorphic rocks containing graphite and phyllosilicates. The simulation of lithostatic pressure was implemented to evaluate conservative conditions for graphene formation. After the experiment, the capsule was characterised by Raman spectroscopy. This analysis aimed to study the diffusion zones between graphite and talc. The characterization technique results provided insights into the chemical composition in different regions of the sample. In the core of the diffusion zone, graphene was detected, evidenced by the significantly higher intensity of the graphite’s 2D band. The experiment was conducted for 24 hours at 700°C to avoid thermal decomposition of talc, with a pressure of 900 MPa, ensuring stable experimental conditions throughout the process.

Finally, Nobre et al. (2023) aims at the technological characterization of this material, analysing how its electrical properties evolve under metamorphic conditions. These observations have significant implications for the practical application of these materials in various industries and research fields. In Nobre et al. (2023) experiment, samples were prepared following the approach adopted in the Nobre et al. (2022b) experiment, with variations in temperature and pressure parameters. To evaluate the electrical properties and gain insights into the conductivity of the samples, resistance tests were performed using a modified two-point method, in which a pair of probes was separated by 1.30 mm. Constant current values were adjusted with a high-precision digital ammeter. This method allowed for obtaining precise measurements of the electrical resistance of the samples, providing a comprehensive understanding of the physical and electrical characteristics of the investigated materials.

4. Discussion

Graphene has sparked great interest from the scientific community in this century, and its implications in geosciences include mineral nanotechnology (Hochella, 2008; Hochella et al., 2008; Nobre et al., 2021), two-dimensional mineralogy (Frisenda et al., 2020; Bindi et al., 2023; Liu et al., 2023), and graphene geology (Hazen et al., 2013; Qu et al., 2019; Vaughan, 2019; Nobre et al., 2022a).

In the simulation of geological graphene formation, the analysis of the experiments revealed that graphite undergoes progressive changes near the talc diffusion zone. Notably, during this process, the stabilisation of graphene on the talc substrate was observed, concentrating mainly in the core of the mentioned diffusion zone. These results indicate that exploring natural graphene deposits in specific geological contexts holds promising potential, providing insights into the material's natural development and potential applications. This simulation provides valuable insights into the natural development of graphene in low-grade metamorphic rocks containing graphite and phyllosilicates.

Furthermore, the research in question has significant implications in the realm of natural graphene extraction and the improvement of mining in the materials industry. This approach not only facilitates technological innovations but also promotes the democratisation of access to advanced technologies on a global scale. The convergence of these advances with the principles of the Fourth and Fifth Industrial Revolution highlights the synergy between scientific research and disruptive transformations in production, positioning the materials industry at the forefront of innovation and sustainability.

5. Conclusions

The analysis of the results allows us to assert the existence of natural graphenes, primarily when considering graphite nanoplates. The dedicated research towards obtaining natural graphene plays a crucial role in enabling large-scale production more economically. By exploring natural sources of graphene, the possibility opens up to identify more efficient and accessible methods for acquiring this revolutionary material. This dedication not only drives technological advancements but also expands opportunities for various applications across different sectors.

The results of Brazilian research studies confirm the possibility of the formation and stabilisation of natural graphene in metamorphic rocks with suitable mineralogy, emphasising the importance of the presence of graphite as a source of graphene and another mineral to serve as a substrate. Experiments under isostatic pressure and temperatures compatible with metamorphic processes in the Earth's crust demonstrate the formation and stabilisation of graphene in talc, indicating that thermodynamic conditions favor graphene formation.

The identified graphene nanoplates stand out as crucial elements in this research scenario. The presence of these two-dimensional structures suggests significant potential for innovative applications, given graphene's known exceptional properties. Understanding the characteristics of graphene nanoplates in different geological contexts contributes to expanding knowledge about the ideal conditions for the formation of these remarkable structures. These findings not only enrich fundamental research in geosciences but also point to possible practical applications in cutting-edge technologies, reinforcing the importance of exploring graphene's unique properties to drive innovations across various sectors.

Furthermore, natural graphene has shown promising industrial applications, as evidenced by studies emphasising the importance of identifying potential target rocks. This discovery plays a crucial role in the nanotechnology industry, providing a valuable raw material for the manufacturing of advanced electronic devices, conductive materials, and other high-tech applications. Understanding the evolution of electrical conductivity in geological contexts significantly contributes to prospecting mineral resources with desirable electrical properties for specific industrial applications. Thus, the results of this research have substantial potential to positively impact the nanotechnology industry, offering crucial insights for the identification and efficient use of mineral resources with favorable electrical properties.

Acknowledgments

The authors are deeply grateful to the Institutional Program for Scientific Initiation Scholarships (PIBIC) through the National Council for Scientific and Technological Development (CNPq) for awarding me the scholarship. Additionally, authors would like to extend my thanks to the research project 060011 - Mineral Nanotechnology at the Federal University of Santa Maria (UFSM) for its support and funding, both of which played a significant role in the development and success of this research.

Conflict of interest

There is no conflict of interest for this study.

References

[1] Ali, S.H.; Al-Sultan, H.A.; Al Rubaie, M.T. Fifth Industrial Revolution. *Int. J. Business, Manag. Econ. Res.* **2022**, *3*, 196–212, https://doi.org/10.47747/ijbme.v3i3.694.

[2] Le Ba, T.; Mahian, O.; Wongwises, S.; Szilágyi, I.M. Review on the recent progress in the preparation and stability of graphene-based nanofluids. *J. Therm. Anal. Calorim.* **2020**, *142*, 1145–1172, https://doi.org/10.1007/s10973-020-09365-9.

[3] Bindi, L.; Zhou, X.; Deng, T.; Li, Z.; Wolverton, C. Kanatzidisite: A Natural Compound with Distinctive van der Waals Heterolayered Architecture. *J. Am. Chem. Soc.* **2023**, *145*, 18227–18232, https://doi.org/10.1021/jacs.3c06433.

[4] Catania, F.; Marras, E.; Giorcelli, M.; Jagdale, P.; Lavagna, L.; Tagliaferro, A.; Bartoli, M. A Review on Recent Advancements of Graphene and Graphene-Related Materials in Biological Applications. *Appl. Sci.* **2021**, *11*, 614, https://doi.org/10.3390/app11020614.

[5] Frisenda, R.; Niu, Y.; Gant, P.; Muñoz, M.; Castellanos-Gomez, A. Naturally occurring van der Waals materials. *npj 2D Mater. Appl.* **2020**, *4*, 1–13, https://doi.org/10.1038/s41699-020-00172-2.
[6] Geim, A.K.; Novoselov, K.S. The rise of graphene. *Nat. Mater.* **2007**, *6*, 183–191, doi:10.1038/nmat1849.
[7] Groumpos, P.P. A Critical Historical and Scientific Overview of all Industrial Revolutions. *IFAC-PapersOnLine* **2021**, *54*, 464–471, https://doi.org/10.1016/j.ifacol.2021.10.492.
[8] Hazen, R.M.; Downs, R.T.; Jones, A.P.; Kah, L. Carbon Mineralogy and Crystal Chemistry. *Rev. Mineral. Geochem.* **2013**, *75*, 7–46, doi:10.2138/rmg.2013.75.2.
[9] Hochella, M.F. Nanogeoscience: From Origins to Cutting-Edge Applications. *Elements* **2008**, *4*, 373–379, https://doi.org/10.2113/gselements.4.6.373.
[10] Hochella, M.F.; Lower, S.K.; Maurice, P.A.; Penn, R.L.; Sahai, N.; Sparks, D.L.; Twining, B.S. Nanominerals, Mineral Nanoparticles, and Earth Systems. *Science* **2008**, *319*, 1631–1635, https://doi.org/10.1126/science.1141134.
[11] Kausar, A.; Ahmad, I.; Eisa, M.H.; Maaza, M. Graphene Nanocomposites in Space Sector—Fundamentals and Advancements. *C* **2023**, *9*, 29, https://doi.org/10.3390/c9010029.
[12] Liu, Q.; Fu, Y.; Qin, Z.; Wang, Y.; Zhang, S.; Ran, M. Progress in the applications of atomic force microscope (AFM) for mineralogical research. *Micron* **2023**, *170*, 103460, https://doi.org/10.1016/j.micron.2023.103460.
[13] Noble, S.M.; Mende, M.; Grewal, D.; Parasuraman, A. The Fifth Industrial Revolution: How Harmonious Human–Machine Collaboration is Triggering a Retail and Service [R]evolution. *J. Retail.* **2022**, *98*, 199–208, https://doi.org/10.1016/j.jretai.2022.04.003.
[14] Nobre, A. G., da Silva, L. P. N., de Andrade, F. R. D. (2022a). Graphene Geology and the Fourth Industrial Revolution. In: Iano, Y., Saotome, O., Kemper Vásquez, G.L., Cotrim Pezzuto, C., Arthur, R., Gomes de Oliveira, G. (Eds.), Proceedings of the 7th Brazilian Technology Symposium (BTSym'21) (Vol. 207, pp. 342–348). https://doi.org/10.1007/978-3-031-04435-9_34
[15] Nobre, A. G., Martínez, J. A. E., Terence, M. C., & Florêncio, O. (2020). The action of shear zones in the natural availability of graphite nanoplatelets: the example of the metadolomites of the Itaiacoca Group and the mica schist of the Dom Silverio Group. Brazilian Journal of Animal and Environmental Research, 3(4), 11. https://doi.org/10.34188/bjaerv3n4-031
[16] Nobre, A.G., Martínez, J. A. E., Florêncio, O. (2021). Mineral nanotechnology in circular economy. In: Iano, Y., Saotome, O., Kemper, G., Mendes de Seixas, A.C., Gomes de Oliveira, G. (eds.). Proceedings of the 6 th Brazilian Technology Symposium (BTSym'21)(Vol. 233, pp. 220–226). https://doi.org/10.1007/978-3-030-75680-2_26
[17] Nobre, A. G., Salazar-Naranjo, A. F., Andrade, F. R. D., Vlach, S. R. F., Ando, R. A. (2022b). Simulation of geological graphene genesis by the piston-cylinder apparatus. Revista Matéria, 27(4), 8. https://doi.org/10.1590/1517-7076-RMAT-2022-0122
[18] Peng, W., Li, H., Hu, Y., Liu, Y., Song, S. (2016). Does silicate mineral impurities in natural graphite affect the characteristics of synthesized graphene? Materials Research Bulletin, 74, 333-339. https://doi.org/10.1016/j.materresbull.2015.10.036
[19] Qu, Z. B., Feng, W. J., Wang, Y., Romanenko, F., Kotov, N. A. (2019). Diverse Nanoassemblies of Graphene Quantum Dots and Their Mineralogical Counterparts. Angewandte Chemie, 132(22): 8620-8629. https://doi.org/10.1002/ange.201908216
[20] Rodrigues, F.C., Nobre A. G., da Silva, E. E., Terence, M. C., Carrió, J. A. (2017). Graphite/Metal Electrodes for Electrochemical Exfoliation: Few Layers Graphene with Low Defects. Defect and Diffusion Forum, 371, 131-134. https://doi.org/10.4028/www.scientific.net/DDF.371.131
[21] Ruiz-Hitzky, E., Darder, M., Fernandes, F. M., Zatile, E. (2011). Supported Graphene from Natural Resources: Easy Preparation and Applications. Advanced Materials, 23(44), 5250-5255. https://doi.org/10.1002/adma.201101988
[22] Vaughan, D. J. (2019). Graphite to Graphene: From a Mineral to an Advanced Technological Material. Elements, 15(3): 215-216. https://doi.org/10.2138/gselements.15.3.215
[23] Walimbe, P., Chaudhari, M. (2019). State-of-the-art advancements in studies and applications of graphene: a comprehensive review. Materials Today Sustainability, 6: 100026. https://doi.org/10.1016/j.mtsust.2019.100026
[24] Wong, C. H. A., Sofer, Z., Pumera, M. (2015). Geographical and Geological Origin of Natural Graphite Heavily Influence the Electrical and Electrochemical Properties of Chemically Modified Graphenes. Chemistry – A European Journal, 21(23), 8435-8440. https://doi.org/10.1002/chem.201500116
[25] Zizic M. C., Mladineo, M., Gjeldum N., Celent, L. (2022). From Industry 4.0 towards Industry 5.0: A Review and Analysis of Paradigm Shift for the People, Organization and Technology. Energies, 15(14), 5221. https://doi.org/10.3390/en15145221