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POTASSIUM RECOVERY FROM PHLOGOPITE MICAS: MECHANISMS, AGRONOMIC POTENTIAL, AND RESEARCH GAPS – A REVIEW

RECUPERAÇÃO DE POTÁSSIO DE MICAS DE FLOGOPITA: MECANISMOS, POTENCIAL AGRONÔMICO E LACUNAS DE PESQUISA – UMA REVISÃO

RECUPERACIÓN DE POTASIO DE MICAS DE FLOGOPITA: MECANISMOS, POTENCIAL AGRONÓMICO Y BRECHAS DE INVESTIGACIÓN – UNA REVISIÓN

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ABSTRACT

Phlogopite, a magnesium-rich potassium mica, has recently gained attention as a potential alternative source of potassium (K) for sustainable agriculture. Unlike conventional fertilizers based on soluble salts such as potassium chloride (KCl), phlogopite is abundant in ultramafic and pegmatitic rocks and can serve as a slow-release K source. This review critically examines the physicochemical properties of phlogopite, its weathering behavior, and its potential agronomic applications. Special emphasis is given to recent advances in thermal, mechanochemical, microbial, and chemical activation techniques that enhance potassium release. Agronomic trials demonstrate promising results across a range of crops and soil conditions. However, several barriers remain, including low natural solubility, high activation energy costs, and limited exploration of global reserves. Research gaps are identified regarding the kinetics of K release under field conditions, the environmental impacts of processing routes, and the scalability of activation technologies. This review highlights phlogopite as a promising resource for transitioning to more resilient, locally sourced K inputs in agriculture.

KEYWORDS: *Phlogopite. Potassium. Mineral solubilization. Sustainable agriculture. Soil remineralization.*

RESUMO

A flogopita, uma mica potássica rica em magnésio, tem ganhado destaque recente como uma fonte alternativa de potássio (K) para a agricultura sustentável. Diferentemente dos fertilizantes convencionais baseados em sais solúveis, como o cloreto de potássio (KCl), a flogopita é abundante em rochas ultramáficas e pegmatíticas e pode atuar como uma fonte de liberação lenta de K. Esta revisão examina criticamente as propriedades físico-químicas da flogopita, seu comportamento de intemperismo e suas potenciais aplicações agronômicas. Ênfase especial é dada aos avanços recentes em técnicas de ativação térmica, mecanocímica, microbiana e química que aumentam a liberação de potássio. Ensaios agronômicos demonstram resultados promissores em diversas culturas e condições de solo. No entanto, persistem vários desafios, incluindo baixa solubilidade natural, altos custos energéticos de ativação e pouca exploração das reservas globais.

PALAVRAS-CHAVE: Flogopita. Potássio. Solubilização mineral. Agricultura sustentável. Remineralização do solo.

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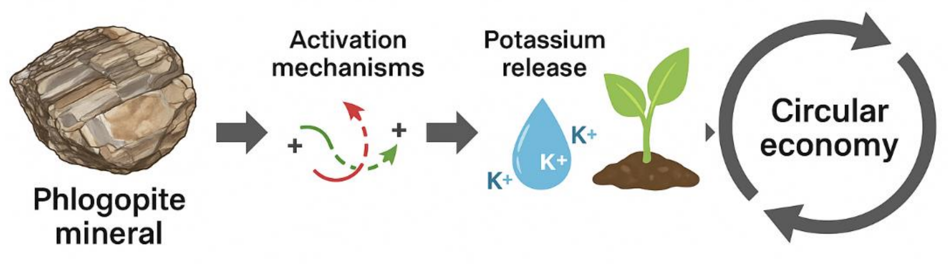
RESUMEN
La flogopita, una mica potásica rica en magnesio, ha recibido atención reciente como una fuente alternativa de potasio (K) para la agricultura sostenible. A diferencia de los fertilizantes convencionales basados en sales solubles, como el cloruro de potasio (KCl), la flogopita es abundante en rocas ultramáficas y pegmatíticas y puede actuar como una fuente de liberación lenta de K. Esta revisión examina críticamente las propiedades fisicoquímicas de la flogopita, su comportamiento frente al intemperismo y sus posibles aplicaciones agronómicas. Se da especial énfasis a los avances recientes en técnicas de activación térmica, mecanoquímica, microbiana y química que mejoran la liberación de potasio. Los ensayos agronómicos muestran resultados prometedores en diversos cultivos y condiciones de suelo. Sin embargo, persisten varios obstáculos, como la baja solubilidad natural, los altos costos energéticos de activación y la limitada exploração de reservas globales. Se identifican brechas de investigación relacionadas con la cinética de liberación de K en condiciones de campo, los impactos ambientales de las rutas de procesamiento y la escalabilidad de las tecnologías de activación. Esta revisión destaca a la flogopita como un recurso prometedor en la transición hacia insumos de K más resilientes y de origen local en la agricultura.

PALABRAS CLAVE: *Flogopita. Potasio. Solubilización mineral. Agricultura sostenible. Remineralización del suelo.*

Highlights

- Phlogopite is a promising alternative potassium source for agricultural use.
- Mechanochemical and biological activation methods can enhance K release.
- Application as a soil remineralizer provides slow-release benefits and reduces leaching losses.
- Economic and environmental feasibility at scale remains a challenge.
- Combining phlogopite with solubilizing microorganisms increases agronomic efficiency.

Graphical abstract



1. INTRODUCTION

Global potash markets remain vulnerable to geopolitical shocks and supply concentration, renewing interest in regional, silicate-based potassium (K) sources and mineral by-products as complementary fertilizers (FAO, 2019; IFA, 2023, 2025; Reuters, 2024; USGS, 2025). Within this scope, K-bearing silicates—especially micas and feldspars—are being revisited as slow/controlled-release inputs and soil remineralizers, with agronomic outcomes governed by mineralogy, processing route, and soil–plant context (Ciceri *et al.,* 2019; Swoboda *et al.,* 2022; Chen *et al.,* 2024). Pot and field studies demonstrate yield and nutrient-use efficiency responses as a function of particle size distribution, activation pathway, and edaphic–microbial interactions (Almeida *et al.,* 2022; Gabira *et al.,* 2022; Lee *et al.,* 2024).

Phlogopite ($KMg_3(AlSi_3O_{10})(F,OH)_2$), a Mg-rich trioctahedral mica, is notable because it combines significant K_2O content with increased susceptibility to vermiculitization and microbial or rhizosphere-mediated alteration compared to muscovite—features that may enhance progressive K mobilization under cultivation (Rezaeinejad *et al.,* 2021; Ashrafi-Saeidlou *et al.,* 2024). Similarly, the bioactivation literature has advanced the use of potassium-solubilizing microorganisms (KSB), such as Aspergillus niger and Bacillus spp., which promote localized acidolysis, chelation, and interlayer expansion, thereby speeding up K release from micas and related minerals (Ashfaq, 2022; Chen *et al.,* 2022; Jafari *et al.,* 2021). For phlogopite, microbial incubation and enriched vermicomposting have shown solubilization and structural transformation. Reviews and applied studies suggest that low-grade mica residues can be bio-upgraded and used as cost-effective potassium (K) sources, especially in developing countries (2022).

From a processing perspective, several activation methods have been evaluated to improve phlogopite reactivity: (i) mechanochemical activation (high-energy milling) to induce structural disorder and increase surface area; (ii) thermal treatments (with or without additives) to promote dehydroxylation and layer reorganization; (iii) alkaline/hydrothermal conditions to accelerate framework disruption and interlayer exchange; and (iv) hybrid bio-mechanical strategies that optimize cost, efficiency, and release profiles (Said *et al.,* 2018; Lodi *et al.,* 2021; Favel; Du Plessis, 2022; Mbissik *et al.,* 2021; Chen *et al.,* 2024). These approaches, used alone or in combination, involve trade-offs in energy consumption, CAPEX/OPEX, and environmental impact, which should be considered within circular-economy scenarios (waste-heat integration, co-product use, reagent recycling), regulatory standards, and decarbonization targets (Buss *et al.,* 2022; Cordeiro, 2024; Leiva *et al.,* 2025; Lyons, 2025; Smol, 2021).

On the agronomic front, activated rocks and micas exhibit crop responses and soil K dynamics influenced by texture, acidity, microbiota, and management, with potential co-benefits such as Mg/Si supply and modulation of P-related microbial processes (Gomes *et al.*, 2019; Almeida *et al.*, 2022; Lee *et al.,* 2024; Zhuang *et al.,* 2024). Simultaneously, improving potassium use efficiency in cereals and enhancing food system resilience drive strategies to reduce dependence on imported KCl and promote regional K sources—assuming performance, safety, and methodological standardization are validated (Dhillon *et al.,* 2019; IFA, 2023, 2025; Lyons, 2025; USGS, 2025). At more detailed levels, synchrotron-based imaging and clay–K interaction studies have advanced our understanding of adsorption, speciation, and microstructural changes during K release (Poonpakdee *et al.,* 2025; Kome *et al.,* 2019; Ghosh *et al.,* 2025).

Aligned with the principles of the Materials Circular Economy, recovering potassium from phlogopite micas provides more than just a sustainable alternative to traditional fertilizers — it represents a closed-loop way to reuse mineral resources. This approach promotes reusing underused silicate minerals in productive ways, which helps reduce dependence on imported soluble salts and decreases waste from mining and processing. By combining mineral activation with industrial symbiosis and lifecycle improvements, phlogopite reuse supports new models for low-carbon materials and circular nutrient management, boosting resource efficiency and climate-resilient farming (Smol, 2021; Cordeiro, 2024; Leiva *et al.,* 2025)

This review provides a critical overview of phlogopite, aiming to: (i) clarify mineralogical and structural factors affecting potassium release; (ii) compare activation methods—mechanical, thermal, alkaline/hydrothermal, biological, and hybrid—and their mechanisms; (iii) summarize leaching chemistry and kinetics; (iv) evaluate agronomic evidence from pot and field studies, including soil–root–microbe interactions; and (v) consider environmental, regulatory, and economic factors that influence scale-up and adoption (Said *et al.,* 2018; Lodi *et al.,* 2021; Favel; Du Plessis, 2022; Swoboda *et al.,* 2022; Leiva *et al.,* 2025; Lyons, 2025).).

2. METHODOLOGY

Literature search strategy

A systematic literature review was conducted to identify peer-reviewed studies, conference proceedings, and institutional reports on phlogopite-based potassium recovery and the agronomic performance of silicate-derived fertilizers. The search spanned from 2017 to 2025 across databases including Scopus, Web of Science, ScienceDirect, and Google Scholar, following the PRISMA 2020 protocol for transparency and reproducibility. Boolean expressions combined keywords such as “phlogopite,” “mica,” “potassium release,” “bioactivation,” “mechanochemical activation,” “hydrometallurgical extraction,” “slow-release fertilizer,” and “soil remineralization.

Grey literature (e.g., FAO, IFA, USGS, and regulatory reports) was included to capture market, regulatory, and policy contexts (FAO, 2019; IFA, 2023, 2025; USGS, 2025). The reference lists of key reviews and experimental studies were manually screened to identify additional relevant works (Basak, 2019; Jena, 2021; Swoboda *et al.,* 2022; Ashrafi-Saeidlou *et al.,* 2024).

Eligibility and inclusion criteria

Studies qualified for inclusion if they met at least one of the following criteria:

a. Investigated phlogopite or biotite as a potassium source under laboratory, greenhouse, or field conditions.

b. Reported mechanisms for activation or solubilization, such as thermal, mechanical, chemical, hydrothermal, or biological methods.

c. Presented data on quantitative K-release, leaching kinetics, or soil–plant responses.

d. Conducted comparative analyses among K-bearing silicates or between natural and processed materials.

e. Explored the circular economy or life-cycle implications of mineral-based fertilizers.

Exclusion criteria

Publications were excluded if they:

a. Focused solely on feldspars, clays, or industrial by-products with no relevance to mica.

b. Lacked experimental or analytical data, such as only relying on theoretical speculation.

c. Were non-English or not peer reviewed.

d. Duplicated datasets from previously published works without adding new interpretation.

Conference abstracts and short communications were included only if they presented original data or methodological innovations (Chen *et al.,* 2024; Lodi *et al.,* 2021).

Data extraction and synthesis

Each chosen publication was examined to gather standardized information across five categories.

(i) Mineralogical and chemical analysis,

(ii) Activation method (for instance, mechanochemical parameters, leaching media, microbial strain),

(iii) K-release performance (mg K/kg sample, rate constants, or cumulative % K_2O release)

(iv) Agronomic outcomes such as biomass, yield, and soil-available K, and

(v) Environmental and economic indicators such as energy consumption, CO_2 footprint, and process scalability.

Quantitative data were normalized where possible and compared across activation types to identify reactivity patterns (Favel; Du Plessis, 2022; Pereira *et al.,* 2025). Qualitative insights were organized thematically, focusing on mechanisms, agronomic effectiveness, and circularity indicators.

PRISMA flow summary

Figure 1 displays the PRISMA 2020-compliant workflow used in this review.

Out of 486 initial records, 327 were screened after removing duplicates; 92 full-text studies met the eligibility criteria, and 61 were finally included in the analysis. Reasons for exclusion included lack of quantitative K data (n = 14), irrelevant mineralogy (n = 9), or language restrictions (n = 8).

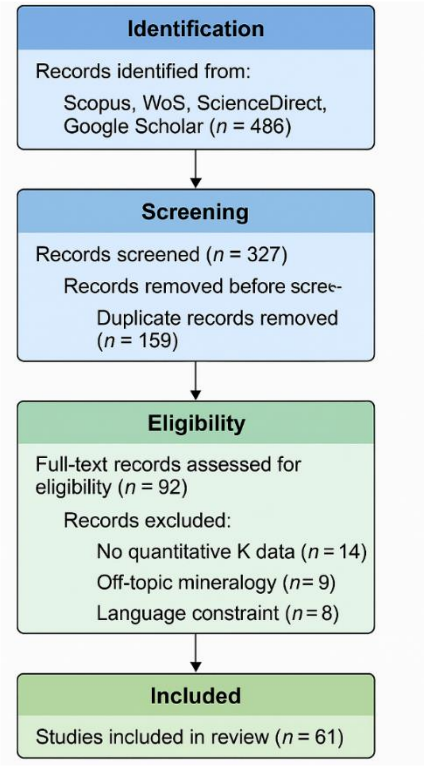


Figure 1. PRISMA flow summary

Methodological reliability and bias control

To minimize selection bias, screening and data extraction were conducted independently by two reviewers, with disagreements resolved through a consensus-based approach. Reference verification and DOI validation ensured data traceability (Dhillon *et al.,* 2019; Lyons, 2025). For missing data, corresponding authors were contacted when possible. The reproducibility of classification criteria follows open-science practices endorsed by the International Fertilizer Association and the FAO (2019).

Link to results section

The following section (Section 3 – Results and Discussion) combines the compiled datasets, comparing activation mechanisms, K-release kinetics, and agronomic performance across different scales—from laboratory dissolution tests to field-based soil remineralization trials.

3. MINERALOGICAL VARIABILITY

The mineralogical variability of phlogopite is crucial in determining its reactivity and the effectiveness with which it releases potassium. Variations in crystal size, level of alteration, and the presence of impurities like biotite and chlorite can significantly affect activation results (Jena, 2021; Hashizume, 2022; Said *et al.,* 2021). As seen with muscovite, careful consideration of structural and compositional factors is essential to identify appropriate processing methods (Pereira *et al.,* 2025).

Phlogopite, a trioctahedral mica, differs from biotite by its higher Mg content and lower Fe ratio, which gives it greater stability and less susceptibility to weathering (Rezaeinejad *et al.,* 2021). It is commonly found in ultramafic and metamorphic settings, often forming large, coherent crystals with significant potential for industrial use (Basak *et al.,* 2021; Mbissik *et al.,* 2021).

Table 1 summarizes the key chemical and physical properties that support the agronomic interest in phlogopite as an alternative source of potassium. Its K_2O content usually ranges from 8 to 11 wt%, comparable to or higher than biotite and slightly below the purest forms of muscovite (Jena, 2021; Chen *et al.,* 2024; Swoboda *et al.,* 2022). The layered monoclinic 2:1 phyllosilicate structure and moderate Mohs hardness (2.5–3) facilitate mechanical comminution, thereby increasing reactive surface area and accelerating K^+ diffusion in soil environments (Lodi *et al.,* 2021).

Table 1. Chemical and physical properties of phlogopite relevant to its use as an alternative potassium source

Property	Description / Typical Value	Reference
Chemical Formula	$KMg_3(AlSi_3O_{10})(F,OH)_2$	Chen et al. (2024)
Potassium Content (K_2O)	8–10% by weight	Jena (2021)
Crystal Structure	Monoclinic, layered 2:1 phyllosilicate	Swoboda et al. (2022)
Color	Yellowish to light brown	Almeida et al. (2022)
Hardness (Mohs scale)	2.5–3	Chen et al. (2024)
Density	2.78–2.85 g/cm³	Swoboda et al. (2022)
Cation Exchange Capacity (CEC)	Moderate to low (5–15 cmolc/kg)	Jena (2021)
Natural Water Solubility	Very low	Swoboda et al. (2022)

Potassium Release Potential	Requires chemical, thermal, or biological activation	Chen et al. (2024)
Presence of Other Elements	Mg, Al, Si, Fe, F, OH	Almeida et al. (2022)
Thermal Stability	Up to ~900 °C before significant decomposition	Jena (2021)

Besides its composition, phlogopite’s low inherent solubility allows for the gradual release of nutrients and reduces the risk of leaching, thereby enhancing its role as a slow-release fertilizer (Basak *et al.,* 2021; Mbissik *et al.,* 2021). These qualities, along with their abundant deposits in tropical and subtropical regions, support its use in soil remineralization programs and circular nutrient strategies (Hinsinger *et al.,* 2021; Cordeiro, 2024).

The similarities between muscovite and phlogopite—particularly their layered crystal structure and strong interlayer K–O bonds—indicate that both minerals face similar challenges in accessing potassium. However, phlogopite’s higher Mg content and lower Fe oxidation potential might give it an edge in bioactivation and mechanochemical treatments, where cation substitution can weaken the structure and promote ion exchange (Jafari *et al.,* 2021; Rezaeinejad *et al.,* 2021).

Figure 2 shows the flat shape and layered 2:1 phyllosilicate structure typical of phlogopite mica. Its monoclinic symmetry is shown in the lower diagram, emphasizing the anisotropic crystal growth along the a and c axes. The stacking of tetrahedral–octahedral–tetrahedral sheets (TOT) explains its easy cleavage, variable hydration, and significant role in potassium release during activation.

From a mineralogical perspective, the figure highlights the anisotropy of phlogopite—strong bonds within the layers and weak interlayer forces between the K^+ cations. This structure governs the accessibility of interlayer potassium, making the mineral responsive to activation treatments such as thermal expansion, mechanochemical milling, or acid leaching. The schematic projection of the crystallographic axes (a and c) effectively illustrates this anisotropy, showing how lattice distortion along the c-axis facilitates the diffusion of ions once the interlayer structure is disrupted.

Figure 2. Crystalline form of phlogopite. Adapted from Chen *et al.* (2024)

Critically, the figure also illustrates why phlogopite is less reactive than muscovite or biotite in its natural state. The stronger Mg–O bonding in the octahedral layer increases structural stability, requiring more energy to release K^+. This visual representation thus connects crystallography and agronomic performance, highlighting that structural configuration—not just chemical composition—controls potassium availability.

Figure 3 shows the main reflections typical of phlogopite mica, including basal planes (001 at 8.8° 2θ and 002 at 17.7° 2θ) and higher-order peaks such as 131 (around 27.9° 2θ) and 060 (around 44.8° 2θ). The natural sample (gray curve) exhibits sharp, well-defined peaks indicating high crystallinity and an organized lamellar structure. In contrast, the activated sample (orange curve) exhibits broader, less intense peaks, indicating partial structural amorphization and disruption of layers resulting from mechanical or thermal activation.

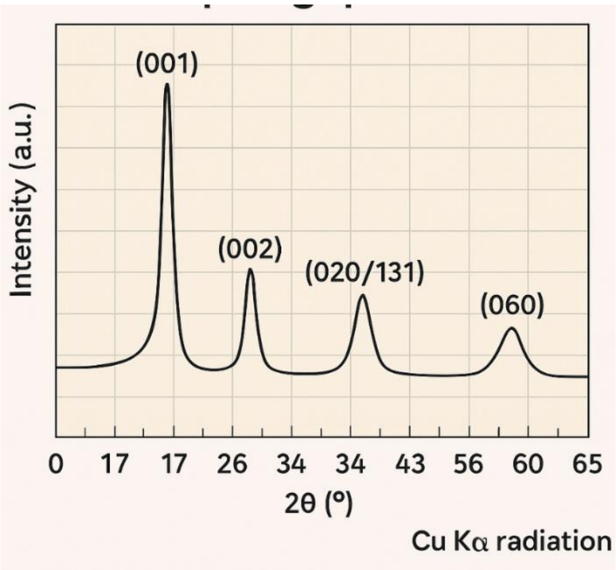


Figure 3. Representative X-ray diffraction pattern of phlogopite (Cu Kα). Adapted from typical mica reference patterns discussed in Jena (2021), Swoboda *et al.,* (2022), and Chen *et al.*, (2024)

This structural change enhances access to interlayer K^+ ions, facilitating the release of potassium during chemical or biological leaching. The movement and broadening of the (001) reflection verify the expansion and partial collapse of the interlayer spacing—an important sign of activation efficiency.

The mineralogical characteristics described above directly affect solubility behavior and activation response. Section 4 (Solubility Limitations) examines the mechanisms that limit potassium release from phlogopite under both natural and treated conditions, with a focus on experimental comparisons and activation thresholds that determine its agronomic effectiveness and viability.

4. SOLUBILITY LIMITATIONS

The low natural solubility of phlogopite in water is a significant limitation to its direct use as a potassium fertilizer. Classical studies have demonstrated that potassium release from phlogopite occurs at much slower rates compared to soluble sources such as potassium chloride (KCl) (Hinsinger *et al.,* 2021; Jena, 2021). This characteristic is related to the strong structural binding of K^+ within the interlayer sites and the high crystalline stability of the mineral (Basak *et al.,* 2021; Lodi *et al.,* 2021).

For example, Rezaeinejad *et al.,* (2021) reported that even under water-stress conditions and intense rhizospheric activity, only a limited fraction of the total potassium is released within agronomically relevant timescales. Jafari *et al.,* (2021) also observed that biological processes, such as enriched vermicomposting with potassium-solubilizing microorganisms, can accelerate potassium release but do not eliminate the intrinsic solubility limitation of phlogopite.

Therefore, phlogopite exhibits a slow-release behavior which, although desirable to reduce leaching losses, requires complementary strategies (mechanical activation, bioactivation, or thermal/acid pretreatments) to achieve potassium availability levels compatible with crop demands (Mbissik *et al.,* 2021; Swoboda *et al.,* 2022).

Figure 4 shows the potassium solubility of three fertilizer types—water-soluble fertilizers, slow-release fertilizers, and natural phlogopite—to highlight the natural reactivity gap that drives activation strategies for phlogopite-based products.

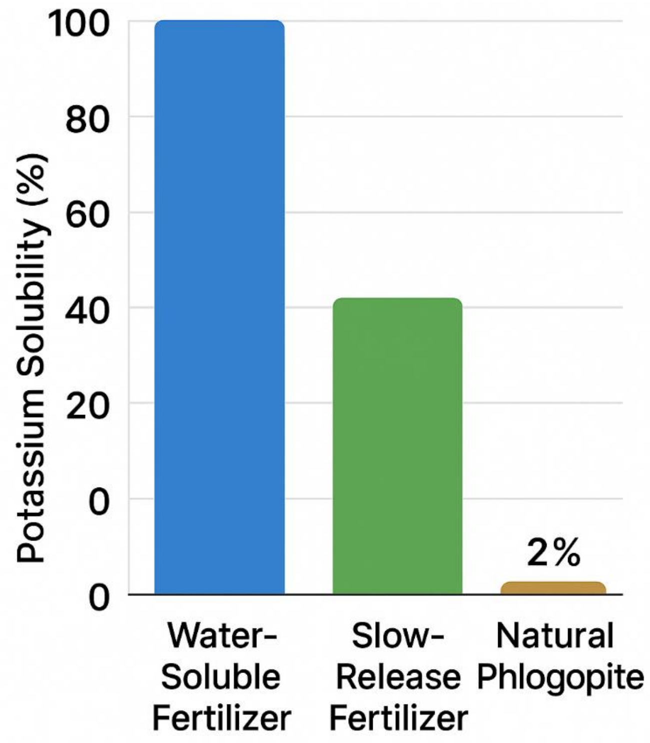


Figure 4. Comparative potassium solubility of fertilizer types. Adapted from Basak *et al.* (2019); Lodi *et al.* (2021); Chen *et al.* (2024)

The graph shows that conventional water-soluble fertilizers (e.g., potassium chloride or potassium sulfate) have nearly 100% solubility, providing immediate potassium availability but also increasing the risk of leaching and nutrient losses.

Slow-release fertilizers, typically derived from partially altered silicates or coated mineral formulations, possess an intermediate solubility of about 50%. This characteristic enables a slow release of K^+, aligning better with plant nutrient uptake and helping to minimize environmental impact.

In contrast, natural phlogopite has an extremely low solubility of about 2% under aqueous conditions (Clemency; May, 1981), reflecting its high crystalline stability and the strength of interlayer K–O bonds. This low natural reactivity limits its direct use in agriculture but emphasizes its potential as a long-term potassium reservoir when subjected to activation treatments such as mechanical milling, hydrothermal leaching, or biological processing, which disrupt the lattice structure and significantly increase potassium availability.

Therefore, the figure highlights the need for activation strategies to close the reactivity gap between phlogopite and conventional fertilizers—balancing nutrient efficiency with environmental sustainability.

Figure 5 shows the logarithmic potassium concentration (ln|K^+|) as a function of solution temperature (°C) for natural and activated phlogopite. The red dashed line indicates the unmodified mineral, which exhibits minimal solubility even at high temperatures due to strong K–O bonds within the interlayer sites and limited diffusion through the phyllosilicate lattice. In contrast, the blue solid line shows increased solubility after structural activation, in which mechanical or chemical disruption of the tetrahedral–octahedral–tetrahedral (TOT) layers exposes interlayer potassium ions to the solution.

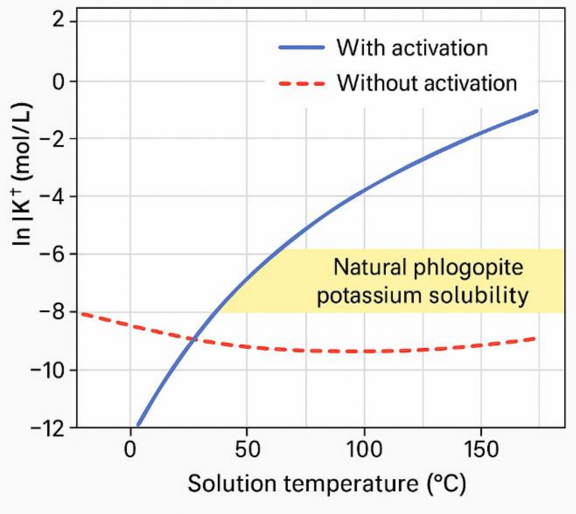


Figure 5. Potassium solubility behavior of phlogopite with and without activation. Adapted from Rezaeinejad *et al.* (2021); Lodi *et al.* (2021); Chen *et al.* (2024); Pereira *et al.* (2025)

The yellow-highlighted band indicates the solubility range of natural phlogopite, confirming its role as a slow-release potassium source. This highlights the need for activation treatments to make phlogopite agronomically useful as a mineral fertilizer.

The analysis presented here strengthens the case for exploring various Phlogopite Activation Routes, which aim to overcome solubility limitations through mechanical, chemical, and biological methods.

5. PHLOGOPITE ACTIVATION PATHWAYS AND REACTIVITY IMPROVEMENT

The naturally low reactivity of natural phlogopite necessitates activation methods to enhance potassium (K^+) release and render it suitable for agricultural use. The main methods studied include mechanochemical activation, chemical or hydrothermal treatment, and biological activation, each varying in complexity, efficiency, and environmental impact (Basak *et al.,* 2021; Ciceri; Allanore, 2018; Mbissik *et al.,* 2021).

Mechanochemical activation

Mechanochemical activation—typically performed by high-energy or planetary milling—reduces particle size, disrupts the layered phyllosilicate lattice, and increases specific surface area, all of which favor K^+ leaching. Studies have demonstrated that ultrafine comminution increases potassium release by up to five times compared to untreated mica (Lodi *et al.,* 2021; Skorina; Allanore, 2018). When combined with microbial inoculation, milling further enhances nutrient solubilization (Basak *et al.,* 2021). However, the method's scalability is limited by its energy demand and equipment wear when treating hard silicate minerals (Mbissik *et al.,* 2021).

Figure 6 demonstrates the mechanochemical activation process of phlogopite through high-energy milling. In this method, intense mechanical stress is applied using rotating grinding media (e.g., steel or ceramic balls) within a planetary or attrition mill. The repeated collisions cause fracture, shear, and compression of the mica layers, leading to a reduction in particle size, the formation of structural defects, and the disruption of the interlayer K^+ sites. These combined effects significantly increase the mineral's specific surface area and reactivity toward dissolution. The diagram illustrates how milling transforms the originally ordered, lamellar structure of phlogopite into partially amorphous fragments, enabling the gradual release of interlayer potassium ions (K^+) when in contact with water or soil solutions.

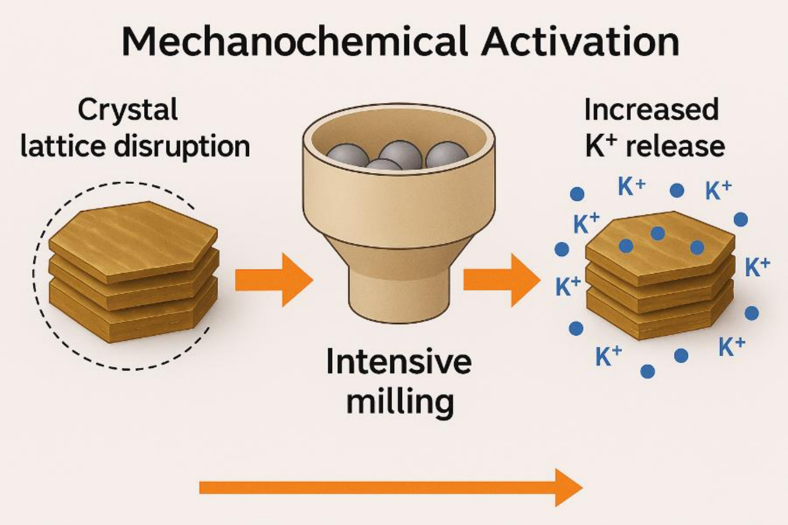


Figure 6. Mechanochemical activation of phlogopite. Adapted from Ciceri & Allanore (2018); Basak *et al.* (2021); Lodi *et al.* (2021)

Mechanochemical activation is one of the most effective methods for increasing the agronomic reactivity of potassium-bearing silicates (Ciceri; Allanore, 2018; Lodi *et al.,* 2021). Its main benefit is that it does not require chemical reagents, making it a more environmentally friendly option compared to acid or thermal activation methods. However, the process requires a high energy input and precise control of milling parameters—such as the ball-to-powder ratio, rotational speed, and milling time—to optimize activation while managing energy costs (Skorina; Allanore, 2018; Mbissik *et al.,* 2021). Overgrinding can lead to excessive amorphization or agglomeration, which decreases solubility gains.

Recent studies have shown that combining mechanochemical treatment with subsequent biological activation or mild hydrothermal processes can further accelerate potassium release while reducing energy consumption (Basak *et al.,* 2021; Swoboda *et al.,* 2022). Therefore, mechanochemical activation should be seen not only as a standalone method but also as an essential pre-treatment that improves the efficiency of subsequent activation routes.

Table 2 summarizes the main physicochemical mechanisms involved in the mechanochemical activation of phlogopite and their respective effects on potassium (K^+) release. The mechanochemical process combines structural disruption and energy-driven reactions that gradually weaken the interlayer bonds typical of 2:1 phyllosilicates. Each stage uniquely influences the mineral's reactivity and its transformation into a more soluble form, making it suitable for agricultural use.

Table 2. Summary of active mechanisms during mechanochemical activation of phlogopite. Adapted from Ciceri and Allanore (2018); Lodi *et al.* (2021); Basak *et al.* (2021); Mbissik *et al.* (2021); Swoboda *et al.* (2022); Chen *et al*. (2024); Jafari *et al.* (2021); Rani *et al.* (2022)

Stage	Main Effect	Impact on K^+ Release
Fracture	Reduction of particle size and increase in surface area	↑ Dissolution rate
Crystal disorder	Creation of lattice defects and vacancies	↑ K^+ mobility
K–O bond rupture	Weakening of interlayer ionic bonds	↑ Direct K^+ liberation
Amorphization	Formation of reactive, partially amorphous surfaces	↑ Chemical reactivity
Biogeochemical synergy	Additional dissolution through organic acids and microbial activity	↑ Process sustainability

The initial stage—fracture—results from the intense compressive and shear forces generated during high-energy milling. These forces significantly reduce particle size and expose new reactive surfaces, leading to faster dissolution kinetics once the material comes into contact with aqueous or acidic media (Ciceri; Allanore, 2018; Lodi *et al.,* 2021). As milling continues, crystal disorder develops, leading to the formation of dislocations and point defects within the lattice. Such distortions decrease the electrostatic retention of K^+ within the interlayer sites, facilitating ion mobility and exchange (Skorina; Allanore, 2018).

A more advanced mechanochemical effect is the breaking of K–O bonds, which directly influences the cohesion between layers in the mica structure. When these bonds are partially broken, the potassium cations become weakly held and more easily released into solution (Basak *et al.,* 2021; Mbissik *et al.,* 2021). With prolonged milling, amorphization occurs—an irreversible structural change that creates disordered regions and amorphous surfaces, which are highly vulnerable to hydration and ion exchange (Swoboda *et al.,* 2022; Chen *et al.,* 2024).

Finally, the biogeochemical synergy stage emphasizes the environmental and agronomic aspects of mechanochemical activation. When the structurally modified phlogopite is added to soils, its high surface area and defect-rich layers boost interactions with root exudates and potassium-solubilizing microbes. These biological processes enhance K^+ dissolution through the action of organic acids and chelating compounds, thereby further increasing nutrient availability (Jafari *et al.,* 2021; Rani *et al.,* 2022).

Overall, the sequence of mechanisms described in Table 2 illustrates that mechanochemical activation is not just a comminution process but a transformative pathway that combines physical fragmentation, crystal disorder, and chemical reactivity. This integrated mechanism explains why mechanically activated phlogopite releases potassium at rates several times higher than the natural mineral, supporting its potential as a low-solubility, slow-release potassium fertilizer.

Chemical and hydrothermal treatments

Chemical activation includes acidic, alkaline, and alkali-hydrothermal processes designed to weaken interlayer bonding and promote ion exchange. Acidic solutions extract interlayer K^+ and leach octahedral cations (Jena, 2021), while alkaline hydrothermal reactions convert phlogopite into amorphous or layered secondary phases (e.g., K-aluminosilicates) with higher solubility (Mbissik *et al.,* 2021). Although thermochemical roasting at temperatures exceeding 800 °C yields high K recovery, it generates significant CO_2 emissions and saline residues (Chen et al., 2024). In contrast, hydrothermal methods under moderate temperatures (150–250 °C) and pressures offer improved environmental performance but require high-pressure reactors and precise control (Swoboda *et al.,* 2022).

Figure 7 presents a comparative overview of the two primary chemical methods investigated for enhancing potassium release from phlogopite: acid/alkaline chemical treatment and alkali-hydrothermal activation. On the left, the chemical treatment path shows how interlayer K–O bonds are broken down by acid (e.g., HCl, H_2SO_4) or alkaline (e.g., NaOH, $Ca(OH)_2$) attacks, leading to partial leaching of structural cations (K^+, Mg^{2+}, Al^{3+}) and the formation of amorphous or secondary silicate phases. On the right, the hydrothermal process depicts high-pressure, high-temperature reactions in alkaline autoclave systems, where phlogopite decomposes into hydrated potassium–magnesium silicates with greater solubility and cation exchange capacity. Both methods seek to weaken the crystalline structure and improve K^+ availability for agricultural use.

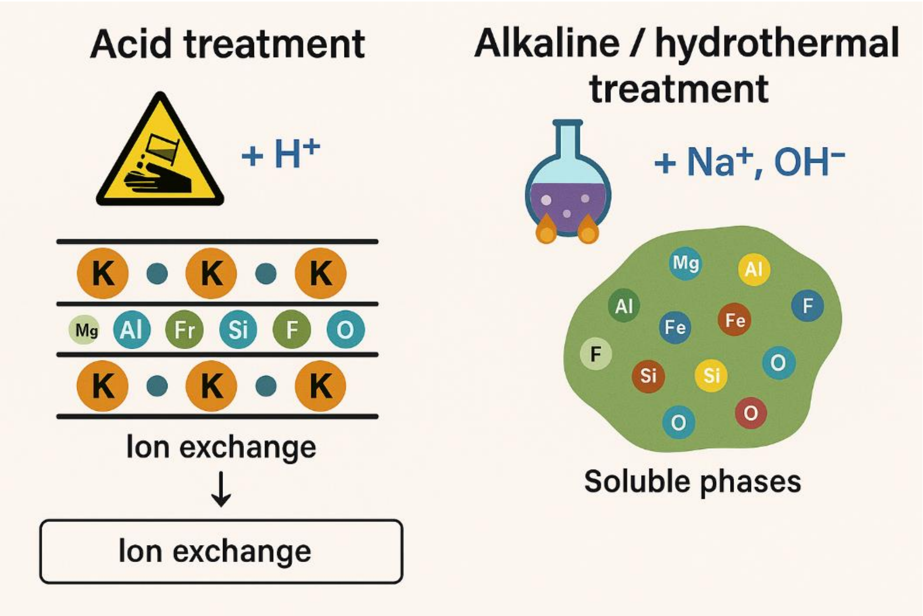


Figure 7. Chemical and hydrothermal treatments for phlogopite activation. Adapted from Ciceri and Allanore (2018), Chen *et al.* (2024), and Mbissik *et al.* (2021)

From a mechanistic perspective, these activation pathways are complementary but vary greatly in energy requirements, environmental effects, and scalability. Acid and alkaline treatments are chemically harsh and can rapidly break down structures; however, they also produce liquid effluents that require neutralization or recycling (Chen *et al.,* 2024; Ciceri; Allanore, 2018). Hydrothermal activation, however, offers a cleaner and more controllable method, with minimal chemical waste and the potential for closed-loop water recovery, albeit at higher capital costs due to the use of autoclave systems (Mbissik *et al.,* 2021; Swoboda *et al.,* 2022).

Recent advances suggest that hybrid processes—combining mild alkaline leaching with hydrothermal treatment—may enhance potassium release efficiencies while minimizing environmental impact (Jena, 2021). The resulting materials exhibit amorphous or semi-crystalline textures, enabling sustained K^+ release and positioning them between soluble and slow-release fertilizers in terms of performance.

Table 3 presents a structured comparison of the chemical and hydrothermal activation methods applied to phlogopite and related potassium-bearing micas. It highlights the main mechanisms, structural changes, and products generated, focusing on how each method influences K^+ release behavior. The table also features a hybrid approach, highlighting the growing interest in combining chemical pre-treatment with hydrothermal reprecipitation for enhanced efficiency.

Table 3. Comparative mechanisms of potassium release in chemical and hydrothermal activation routes. Adapted from Favel & Du Plessis (2022); Pereira & Fonseca (2025); Mbissik *et al.* (2021); Ciceri *et al.* (2019); Jena (2021); Samantray *et al.* (2022).

Activation Route	Main Mechanism	Structural Effect	Product Formed	K^+ Release Behavior
Chemical Treatment (Acid / Alkaline)	Ion exchange and dissolution of interlayer K^+ through acid or base attack.	Partial breakdown of tetrahedral–octahedral–tetrahedral layers; formation of surface defects and vacancies.	Amorphous Si–Al–Mg gels; hydrated silicate residues.	Fast initial leaching; high solubility but risk of effluent generation.
Acidic Leaching (HCl, H_2SO_4)	Proton-driven rupture of K–O and Si–O–Al bonds.	Disorganization of phlogopite lattice; structural collapse and amorphization.	Al–Si gel layer; amorphous aluminosilicates.	Rapid K^+ release under controlled pH; limited by diffusion through the altered layer.
Alkaline Treatment (NaOH, $Ca(OH)_2$)	Nucleophilic substitution and deprotonation; desilication and delamination.	Generation of microporous frameworks and increased specific surface area.	Layered K–Al–Si hydroxides; alkali aluminosilicate residues.	Moderate release rate; improves K accessibility and enhances cation-exchange capacity.
Hydrothermal Activation	High-temperature hydrolysis and	Transformation to vermiculite-like or	Potassium aluminosilicat	Sustained, long-term K^+

(Alkali-Hydrothermal)	recrystallization of phlogopite into reactive hydrated silicates.	amorphous phases with expanded basal spacing.	e gels; Mg–Si–K hydrated phases.	diffusion; slow-release fertilizer behavior.
Hybrid or Sequential Process (Chemical + Hydrothermal)	Pre-leaching followed by hydrothermal reprecipitation to enhance reactivity and reduce waste.	Combined dissolution–recrystallization cycle producing amorphous K–Al–Si matrices.	Mixed amorphous phases with high exchange capacity.	Controlled release with reduced environmental footprint; suitable for circular fertilizer design.

From a mechanistic perspective, acid and alkaline treatments (Favel; Du Plessis, 2022; Pereira; Fonseca, 2025) rely on ion exchange and lattice dissolution, resulting in the rapid extraction of potassium through proton attack and desilication reactions. These methods are effective for immediate nutrient availability but tend to generate liquid effluents that need neutralization or recycling, which reduces their environmental appeal.

In contrast, the hydrothermal route (Mbissik *et al.,* 2021; Ciceri *et al.,* 2019) involves solid-state hydrolysis and recrystallization, resulting in the formation of amorphous or vermiculite-like K–Si–Al phases that facilitate the gradual release of nutrients. This slow-release feature supports circular economy goals, as it reduces leaching and boosts long-term soil fertility. The hydrothermal process also enables closed-loop operation and reuse of process water, but it requires more energy due to pressurized conditions.

The hybrid approach, which combines gentle chemical pre-treatment followed by hydrothermal activation, is emerging as a balanced strategy both technically and environmentally (Jena, 2021; Samantray *et al.,* 2022). It enhances lattice disruption during leaching and promotes the reprecipitation of amorphous potassium-rich silicates, resulting in increased K^+ availability without the need for excessive reagents.

Overall, the table emphasizes the trade-off between kinetic efficiency and environmental sustainability, identifying hydrothermal or hybrid routes as the most promising options for future eco-efficient potassium fertilizers derived from phlogopite.

Biological activation

Bioactivation depends on potassium-solubilizing bacteria (KSB) and filamentous fungi, such as Aspergillus niger, which secrete organic acids and chelating agents to weather the TOT layers of phlogopite (Hinsinger *et al.,* 2021; Rani *et al.,* 2022). Additionally, vermicomposting improves mineral transformation through enzymatic oxidation and microbially driven processes (Jafari *et al.,* 2021). Although slower than chemical activation, biological treatments are sustainable, low-cost, and compatible with organic farming. Their main limitations include reliance on environmental conditions and the need to sustain active microbial populations (Basak *et al.,* 2021).

Figure 8 depicts the biological activation process of phlogopite mica, emphasizing the interaction between microorganisms, root exudates, and mineral weathering in the soil environment. Potassium-solubilizing bacteria (KSB) and filamentous fungi attach to the mineral surface, secreting organic acids, chelators, and extracellular enzymes that penetrate the interlayer spaces of phlogopite. These reactions facilitate the exchange and leaching of interlayer K^+ ions, gradually breaking down the crystalline structure into vermiculite or amorphous residues. Root exudates—particularly citric, oxalic, and malic acids—further promote the dissolution by acidifying the microenvironment and forming complexes with structural cations (Fe^{3+}, Mg^{2+}, Al^{3+}).

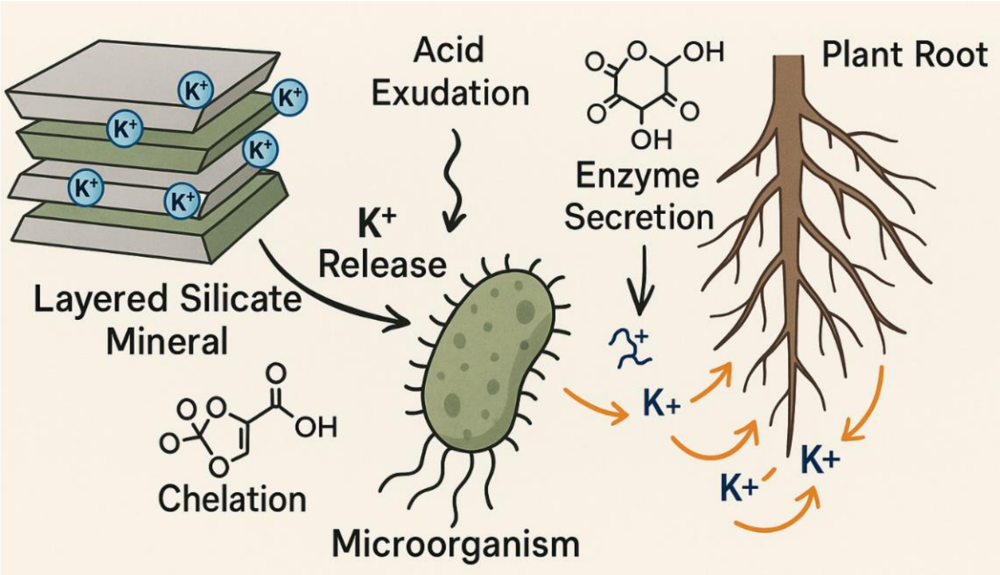


Figure 8. Biological Activation of Phlogopite for Potassium Release. Adapted from**:** Basak *et al.* (2021); Rani *et al.* (2022); Jafari *et al.* (2021); Ashrafi-Saeidlou *et al.* (2024); Fomina & Skorochod (2020); Zhuang *et al.* (2024)

From a biogeochemical perspective, this process offers a sustainable and low-energy alternative to physicochemical activation. Unlike mechanochemical or hydrothermal methods, biological activation depends on synergistic interactions among soil, microbes, and minerals, mimicking natural weathering processes that can be leveraged for agricultural benefits. Studies such as those by Basak *et al.* (2021), Rani *et al.* (2022), and Ashrafi-Saeidlou *et al.* (2024) have demonstrated that inoculation with K-solubilizing microorganisms significantly increases K^+ release, though at a slower pace compared to thermal or chemical methods.

However, the main limitations of this approach involve dependence on environmental factors (temperature, moisture, pH) and maintaining microbial activity in field conditions. The conversion efficiency relies on both particle fineness—which increases surface area and microbe–

mineral contact—and microbial diversity, which determines the range of metabolic pathways available for dissolution.

In summary, biological activation is a green method for recovering potassium from phlogopite and other silicate minerals. Although it is less immediate than chemical or mechanochemical approaches, it provides a sustainable long-term strategy for creating biofertilizers that promote nutrient recycling and improve soil health.

Table 4 summarizes the biogeochemical mechanisms responsible for potassium (K^+) release from phlogopite under biological activation, integrating microbiological, chemical, and mineralogical perspectives. Unlike purely mechanical or chemical approaches, this process is driven by microbial metabolism and rhizosphere interactions, which work together to destabilize the mineral lattice through natural weathering pathways.

Table 4. Mechanisms of potassium release by biological activation of phlogopite. Adapted from Basak *et al.* (2019, 2021, 2022); Jafari *et al.* (2021); Rani *et al.* (2022); Fomina & Skorochod (2020); Rezaeinejad *et al.* (2021); Ashrafi-Saeidlou *et al.* (2024); Zhuang *et al.* (2024)

Stage	**Primary Effect**	**Mechanism**	**Impact on K^+ Release**
1. Microbial colonization	Formation of biofilm on mineral surface	Adherence of *Bacillus* spp. and *Aspergillus* spp. to phlogopite creates localized microenvironments rich in CO_2 and organic acids	Initiates localized dissolution of interlayer K^+ (Basak et al., 2021; Chen et al., 2022)
2. Acidification of microenvironment	Decrease in pH near mineral–microbe interface	Secretion of organic acids (citric, oxalic, malic, gluconic) and H^+ ions weakens interlayer bonds	Promotes rupture of K–O bonds and increases ion mobility (Basak et al., 2019; Rani et al., 2022)
3. Chelation and ligand exchange	Complexation of Fe^{3+}, Mg^{2+}, and Al^{3+} in the structure	Microbial chelators and metabolites destabilize octahedral/tetrahedral sheets	Enhances solubilization and initiates vermiculitization (Fomina & Skorochod, 2020; Rezaeinejad et al., 2021)
4. Enzymatic oxidation–reduction	Modification of mineral surface oxidation state	Enzyme-mediated Fe/Mn redox reactions and microfracturing of lattice sites	Increases reactive surface and accelerates weathering (Zhuang et al., 2024; Moran & McGrath, 2021)
5. Structural transformation	Progressive alteration to vermiculite-like phase	Sustained leaching and ion exchange replace interlayer K^+ with hydrated cations	Converts phlogopite into amorphous residues with higher K availability (Jafari et al., 2021; Ashrafi-Saeidlou et al., 2024)
6. Rhizosphere synergy	Root exudates enhance microbial activity	Combined plant–microbe processes boost acidolysis and complexolysis	Sustained, eco-friendly K^+ release under field conditions (Basak et al., 2021; Lee et al., 2024; Zhuang et al., 2024)

The process begins with microbial colonization on the mineral surface. Potassium-solubilizing microorganisms, such as Bacillus aryabhattai, Aspergillus niger, and Paenibacillus mucilaginosus, adhere to the phlogopite flakes, forming biofilms that concentrate CO_2 and organic acids. This localized microenvironment results in acidification of the mineral–microbe interface, promoting the dissolution of structural cations and weakening the interlayer K–O bonds. These mechanisms were confirmed by Basak *et al.* (2019, 2021) and Ashrafi-Saeidlou *et al.* (2024), who reported significant increases in K^+ release when microbial inoculants were combined with fine mineral particles.

Subsequently, chelation and ligand exchange reactions dominate the dissolution process. Microbial exudates, especially organic acids and siderophores, form complexes with Fe^{3+}, Mg^{2+}, and Al^{3+} in the tetrahedral and octahedral sheets, destabilizing the crystal lattice and triggering partial vermiculitization. Fomina and Skorochod (2020) demonstrated that such chelating activity promotes the transformation of mica minerals into more reactive silicate phases, resulting in increased nutrient availability.

Enzymatic and redox reactions further enhance this process by altering the oxidation states of Fe and Mn species within the structure, resulting in the formation of microfractures and reactive sites. These reactions, as described by Zhuang et al. (2024) and Moran and McGrath (2021), are particularly important in biologically active soils with fluctuating redox conditions. The final phase, structural transformation, involves the gradual conversion of phlogopite into vermiculite-like or amorphous residues, which effectively releases K^+, Mg^{2+}, and Fe^{2+} ions that become accessible to plants (Jafari *et al.,* 2021; Rezaeinejad *et al.,* 2021).

A key point highlighted in the table is the rhizosphere synergy, where plant root exudates—containing organic acids, amino acids, and sugars—boost microbial activity and sustain K^+ release over time. This interaction highlights the eco-functional aspect of biological activation, as it mimics natural soil weathering processes while preserving soil structure and biodiversity (Lee *et al.,* 2024; Basak *et al.,* 2021).

From a critical perspective, although the biological activation route is slower in releasing K^+ than thermal or hydrothermal methods, it offers a sustainable and energy-efficient approach that supports nutrient cycling, soil regeneration, and carbon sequestration. Its main challenges include managing environmental factors such as temperature, pH, and humidity, as well as maintaining active microbial populations in field conditions. Nonetheless, this approach aligns with the principles of the circular economy and can serve as a foundation for developing biofertilizers in low-input agricultural systems.

In summary, the table highlights that biological activation is not a single mechanism but a sequence of interconnected biogeochemical processes—acidolysis, complexolysis, chelation, and redox alteration—each contributing to the gradual but sustainable mobilization of potassium from phlogopite.

Integrated activation strategies

Recent research advocates for integrated approaches, combining mechanochemical pre-treatment with biological or mild hydrothermal activation to synergistically accelerate K^+ release while minimizing energy use (Ciceri; Allanore, 2018; Lodi *et al.,* 2021). Figure 5 summarizes these activation pathways and their role in transforming phlogopite into a reactive potassium source.

Figure 9 illustrates the conceptual framework of integrated activation strategies designed to enhance potassium (K^+) release from phlogopite while minimizing energy consumption and environmental impact. These strategies combine mechanochemical, biological, and hydrothermal processes in complementary sequences, utilizing their respective strengths to overcome the inherent crystalline stability of phlogopite.

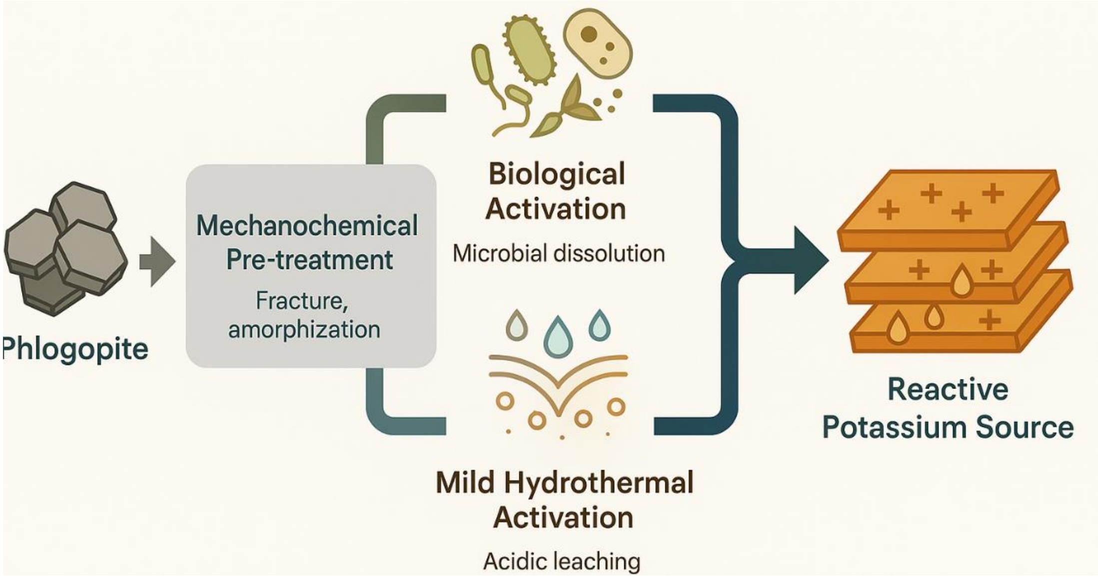


Figure 9. Integrated activation strategies for phlogopite. Adapted from Ciceri & Allanore (2018); Lodi *et al.* (2021); Mbissik *et al.* (2021); Basak *et al.* (2021); Rani *et al.* (2022); Ashrafi-Saeidlou *et al.* (2024)

In the mechanochemical stage, high-energy or ultrafine grinding breaks apart the layered phyllosilicate structure, increasing surface area and creating structural defects. These defects enhance access to interlayer potassium and expose reactive sites, which in turn facilitate chemical and microbial interactions. Studies by Ciceri and Allanore (2018) and Lodi *et al.* (2021) showed that mechanical activation alone can significantly increase potassium dissolution rates, though energy use remains a major limitation at an industrial scale.

The biological component creates a synergistic effect through potassium-solubilizing microorganisms (KSM), such as Aspergillus niger and Bacillus aryabhattai. These organisms release organic acids and chelating agents that speed up potassium leaching from activated mineral surfaces. Combined with prior mechanical activation, bioinoculation leads to improved ion exchange and structural changes under normal conditions, effectively simulating natural weathering processes in a shorter timeframe (Basak *et al.,* 2021; Ashrafi-Saeidlou *et al.,* 2024; Rani *et al.,* 2022).

The mild hydrothermal stage, operating at moderate temperatures (150–250 °C), further improves dissolution by promoting phase transitions without significant energy use or melting. It transforms phlogopite into partly amorphous aluminosilicate structures with greater cation-exchange capacity and solubility. Research by Mbissik *et al.* (2021) demonstrated that such hydrothermal environments facilitate both ion-exchange reactions and alkaline leaching, resulting in the formation of potassium-rich amorphous gels that dissolve readily under soil conditions.

From a technological standpoint, integrating these routes signifies a shift from isolated process optimization to multistage, synergistic activation frameworks. Mechanochemical activation enhances structural accessibility, biological activation promotes sustainability and selectivity, and hydrothermal treatment increases chemical transformation efficiency. The combined effect leads to improved K^+ mobilization, shorter process times, and greater Agronomic efficiency is enhanced compared to single-route activation. Critically, this integrated approach aligns with the principles of green chemistry and circular economy, as it enables the valorization of abundant but low-grade potassium-bearing minerals. However, practical implementation still requires optimization of energy balance, microbial stability, and process scalability. Incorporating renewable energy for milling and bioreactor systems could further decrease the carbon footprint and operational costs, supporting the development of next-generation eco-efficient K fertilizers.

In summary, the figure illustrates how combining mechanical disruption, microbial weathering, and mild hydrothermal alteration can synergistically transform phlogopite into a reactive, slow-release potassium source, thereby bridging the gap between material activation efficiency and sustainable agricultural practices.

Perspectives and Comparative Overview

Each route involves critical trade-offs:

- Release rate: thermochemical > hydrothermal ≈ mechanical > biological
- Sustainability: biological > hydrothermal ≈ mechanical > thermochemical
- Operational costs: biological ≈ mechanical < hydrothermal < thermochemical

In the context of sustainable agriculture, combined approaches—such as mechanical activation followed by biological activation—appear to be the most promising, offering a balance between agronomic efficiency and economic feasibility (Mikkelsen; Roberts, 2021; Swoboda *et al.,* 2022). Additionally, integrating industrial residues (e.g., silica-rich sludges or biomass) has been proposed as a means to reduce costs and environmental impact (Almeida *et al.,* 2022).

Figure 10 shows the relative potassium solubility of phlogopite after various activation treatments, with potassium chloride (KCl) used as the benchmark for 100% solubility. The addition of natural phlogopite (≈2%) provides a baseline, illustrating the mineral's low intrinsic reactivity in aqueous conditions due to its strong interlayer K–O bonds and high crystallinity (Ciceri; Allanore, 2018; Pereira *et al.,* 2021).

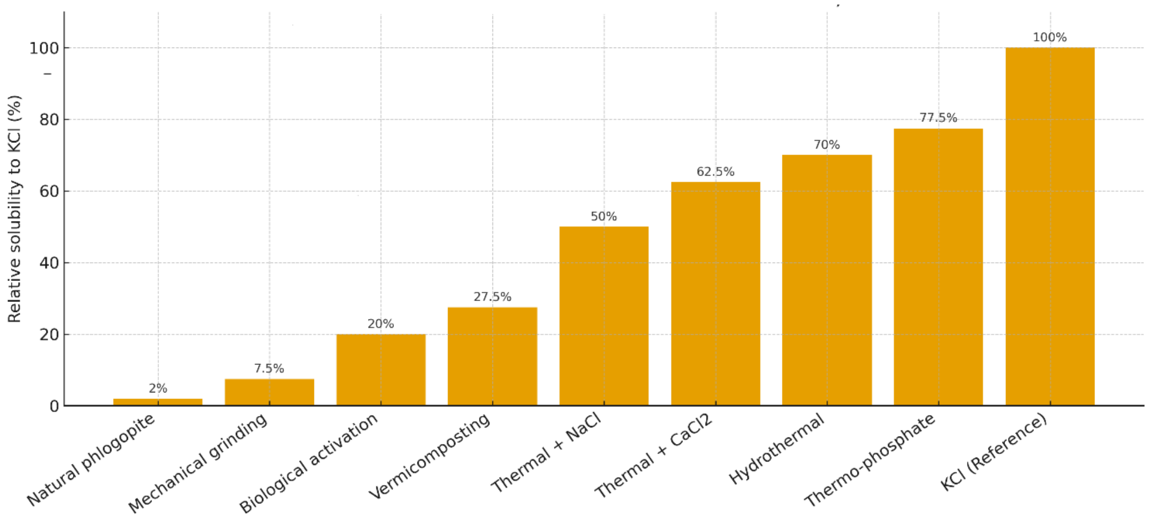


Figure 10. Relative solubility of potassium from phlogopite by activation route. Adapted from: Ciceri & Allanore (2018); Chen *et al.* (2024); Mbissik *et al.* (2021); Lodi *et al.* (2021); Basak *et al.* (2021); Jafari *et al.* (2021); Pereira & Fonseca (2025); Said *et al.* (2018)

The mechanical activation route (7.5%) results in a moderate increase in solubility, attributed to lattice distortions and surface area expansion, as demonstrated in mechanochemical studies by Said *et al.* (2018) and Lodi *et al.* (2021). However, the enhancement is still limited by the retention of crystalline order.

Biological activation (20%) and vermicomposting (27.5%) demonstrate the role of microbial and organic acid-mediated weathering, where microorganisms such as Aspergillus niger and potassium-solubilizing bacteria (KSB) facilitate localized dissolution through organic acids and chelation processes (Basak *et al.,* 2021; Jafari *et al.,* 2021; Ashrafi-Saeidlou *et al.,* 2024).

Among chemical and thermal treatments, the NaCl-assisted thermal process (50%) and $CaCl_2$-assisted roasting (62.5%) show higher efficiencies, linked to ion exchange reactions and chloride-promoted lattice disruption, consistent with the mechanisms described by Chen *et al.*

(2024) and Gomes *et al.* (2019). Hydrothermal activation (70%) further improves solubility by producing amorphous K-bearing phases (Mbissik *et al.,* 2021), while thermo-phosphate treatments (77.5%) mimic the behavior of commercial KCl fertilizers, achieving the greatest increase in K^+ release among solid-phase methods (Becheleni *et al.,* 2019; Pereira; Fonseca, 2025).

Overall, the figure highlights the synergistic potential of combining mechanical, hydrothermal, and biochemical activation methods, enabling the gradual transformation of phlogopite into a slow-to-moderate release potassium source suitable for sustainable agriculture. This trend aligns with recent advances in green fertilizer development and the circular economy approach to nutrient recovery (Cordeiro, 2024; Bouhia *et al.,* 2022; Swoboda *et al.,* 2022).

This overview emphasizes that choosing a route involves balancing cost, sustainability, and the need for rapid potassium release. In organic farming or controlled-release strategies, even biological routes can be appealing (Swoboda *et al.,* 2022).

Potassium Release

The release of potassium (K) from phlogopite is affected by several interconnected factors, including its crystallographic properties (layer spacing, 2:1 mica structure), the presence of associated elements (such as Mg, Fe, F) in the structure, the extent of prior weathering or alteration, and the type of activation method used (e.g., mechanical, chemical, biological) (Jena, 2021; Favel; Du Plessis, 2022).

The main ways K^+ is released from phlogopite involve a mix of physicochemical dissolution (proton or ligand attack, interlayer cation exchange, structural breakdown) and structural changes (such as vermiculitization, amorphization), which free interlayer K and improve its mobility (Ashrafi-Saeidlou *et al.,* 2024; Rezaeinejad *et al.,* 2021).

In mechanochemical activation, for example, intense milling causes fracturing, increases surface area, creates lattice defects, and forms micro-vacancies, which then speed up the dissolution and diffusion of K^+. Thermal and hydrothermal treatments break down the mica structure, promote the release of structural K, and lead to the formation of more reactive phases (Ciceri *et al.,* 2019; Chen e*t al.,* 2024). Biological activation, through K-solubilizing fungi or bacteria and rhizosphere roots under stress, also contributes by producing organic acids or excreting chelators that target interlayer K and may break down mica into vermiculite-type phases (Jafari *et al.,* 2021; Ashrafi-Saeidlou *et al.,* 2024).

Release kinetics are often described by diffusion-layer models and are affected by specific surface area and particle size (Favel; du Plessis, 2022). Intensive milling combined with moderate acidulation tends to favor immediate K availability, whereas thermo-phosphate and hydrothermal activation produce materials with controlled, gradual release (Jena, 2021; Said *et al.,* 2018).

This behavior is important both agronomically, for sustained nutrient supply and reduced leaching, and environmentally, as slow-release fertilizers are especially valued in organic and low-input farming systems (Buss *et al.,* 2022; Swoboda *et al.,* 2022).

Table 5 summarizes the main physicochemical and biological factors that control potassium release from phlogopite, incorporating recent experimental results and mechanistic insights from 2018 to 2025. The data show that crystallographic constraints—especially the strong electrostatic K–O bonds in the interlayer sites of the 2:1 trioctahedral structure—are the main limit to solubility in the mineral's natural state, resulting in very low K release (< 2%) even after long-term exposure to water (Favel; Du Plessis, 2022; Jena, 2021). This explains why unaltered phlogopite does not perform well as a direct fertilizer, and it needs to be activated beforehand to increase nutrient availability.

Table 5. Factors influencing potassium release from phlogopite and associated mechanisms. Adapted from: Said *et al.* (2018); Favel & Du Plessis (2022); Jafari *et al.* (2021); Rezaeinejad *et al.* (2021); Ashrafi-Saeidlou *et al.* (2024); Chen *et al.* (2024); Gomes *et al.* (2019); Mbissik *et al.* (2021); Lodi *et al.* (2021); Pereira & Fonseca (2025)

Factor	Mechanism / Effect	Impact on K Release
Crystallographic structure (2:1 trioctahedral mica)	Strong interlayer K–O bonding; limited ion exchange capacity	Very low solubility in natural state (≈2% K release)
Associated elements (Mg, Fe, F)	Substitution modifies layer charge and K fixation energy	Mg substitution favors vermiculitization; F reduces hydration
Particle size and surface area	Smaller particles enhance diffusion and surface dissolution	Faster initial release; increased kinetics under acid or bio-attack
Weathering degree / pre-alteration	Formation of vermiculite, Fe-oxides, and amorphous gels	Higher reactivity and exchangeable K fraction
Mechanical activation (milling)	Lattice disorder, increased defects, amorphization	Up to 7–10× K release compared to untreated samples
Thermal activation / chlorination	Disrupts layer structure and promotes ion exchange with Cl^-	40–60% K release; forms K-bearing amorphous silicates
Hydrothermal activation	Alkali or water vapor attack; leaching of interlayer K	60–70% K release; enhanced by NaOH or $CaCl_2$ media
Acid leaching (HNO_3, H_2SO_4)	Proton attack on octahedral sheets and interlayer sites	Fast dissolution; >50% K release at optimized conditions
Biological activation (fungi, bacteria)	Organic acids (citric, oxalic) and chelation processes	Moderate K solubilization (10–25%) with structural alteration
Vermicomposting / root exudates	Biotransformation to vermiculite via hydration and oxidation	Sustained slow release; increased cation exchange capacity
Combined mechanical + biological routes	Synergistic: higher reactivity + microbial weathering	Cumulative release up to 16–20% K over 90 days

From a mechanistic perspective, three main pathways emerge: (i) structural disruption, through mechanical, thermal, or hydrothermal energy inputs that weaken interlayer bonds; (ii) chemical attack, via acids or chloride ions that replace or dissolve interlayer cations; and (iii) biochemical alteration, where fungi or bacteria excrete organic acids that complex Mg^{2+} and Fe^{3+}, promoting layer expansion and transformation into vermiculite. These processes differ in efficiency, kinetics, and agronomic relevance. Mechanical activation through high-energy milling significantly increases the surface area and defect density, thereby enhancing initial K diffusion but requiring a substantial energy input (Said *et al.,* 2018; Lodi *et al.,* 2021). Conversely, acid or chloride treatments enable rapid solubilization (> 50% total K released) but may produce effluents needing neutralization (Favel; Du Plessis, 2022; Gomes *et al.,* 2019). Hydrothermal methods offer intermediate levels of solubilization (≈ 60–70%) and maintain a slow-release property desirable for agronomic applications (Mbissik *et al.,* 2021; Chen *et al.,* 2024).

Biological and vermicomposting methods, although less aggressive, are environmentally friendly and can gradually convert phlogopite into vermiculite-like phases with enhanced cation-exchange capacity. However, their kinetic limitations—generally achieving < 25% K release after months of incubation—limit their use as sole treatments (Ashrafi-Saeidlou *et al.,* 2024; Jafari *et al.,* 2021). Hybrid approaches, combining mechanochemical pretreatment with microbial inoculation, have recently shown promising synergy, achieving total releases of up to 16–20% K over 90 days while preserving the environmental safety of the biological process (Ashrafi-Saeidlou *et al.,* 2024).

Notably, the table highlights that the transformation of phlogopite into a reactive, slow-release K source depends on both structural disorder and the chemical environment during activation. Methods that balance these factors—such as moderate-temperature hydrothermal or thermophosphate activation—provide the best compromise between efficiency, scalability, and ecological compatibility. Future efforts should focus on optimizing these integrated routes, assessing their energy balance, agronomic efficiency, and field-scale reproducibility (Basak *et al.,* 2022; Cordeiro, 2024; Swoboda *et al.,* 2022).

6. AGRONOMIC APPLICATIONS OF PHLOGOPITE

From an agronomic perspective, utilizing phlogopite as a potassium source offers potential benefits in circular nutrient systems and low-input agriculture, particularly in areas with limited access to conventional Potassium Fertilizers (Dhillon *et al.,* 2019; Basak *et al.,* 2022). The slow-release nature of activated phlogopite may help reduce leaching and enhance nutrient use efficiency in crops. For environmental sustainability, transforming a naturally abundant mica into a functional fertilizer aligns with broader frameworks of recycled nutrient use and rock dust remineralization strategies (Cordeiro, 2024; Buss *et al,* 2022).

However, significant constraints still exist, including energy intensity, the cost of milling or thermal processing, the scalability of biological activation, variability in mineral sources, and regulatory frameworks for non-conventional fertilizers (Grams; Rehwaldt, 2025).

Table 6 summarizes the agronomic responses to phlogopite application across various crops, drawing on evidence from recent experimental studies (2017–2025). Overall, adding ground, activated, or bio-enhanced phlogopite—either alone or combined with organic residues and microbial bioactivators—has demonstrated measurable benefits for crop growth, soil potassium (K) availability, and nutrient cycling efficiency.

Table 6. Agronomic Applications of Phlogopite and Observed Results. adapted from Pereira *et al.* (2021); Rani *et al.* (2022); Buss *et al.* (2022); Gabira *et al.* (2022); Lodi *et al.* (2021); Ashrafi-Saeidlou *et al.* (2024); Said *et al.* (2018); Souza *et al.* (2017); Basak *et al.* (2022); Cordeiro (2024)

Crop	Treatment / Application Method	Observed Effects
Rice	Phlogopite mixed with plant residues	Yield increase; improved soil fertility and K retention
Lettuce	Phlogopite + mineral-enriched biochar	Significant yield gain; improved water and nutrient use efficiency
Mimosa scabrella	Controlled-release phlogopite remineralizer fertilizer	Enhanced seedling growth, rooting, and soil K availability
Sorghum	Bio-weathering by Aspergillus niger + soil application	Increased K solubilization and higher plant uptake
Common bean	Ground phlogopite incorporated into soil	Improved K uptake; yield comparable to soluble sources long-term
Soybean	Powdered phlogopite and biotite	Supplementation of K and micronutrients; yield enhancement
Maize	Ground phlogopite incorporated into soil	Increased biomass production, higher K uptake, positive residual effect
Tomato	Phlogopite mixed with organic residues	Higher productivity; improved soil chemical and physical properties
Wheat	Thermally activated phlogopite	Controlled K release, positive residual effects, improved soil chemistry
Centrosema (Legume)	Ultramafic rock and phlogopite as K sources	Increased green biomass; improved nutritional balance

In cereal crops such as rice, maize, and wheat, applying phlogopite—especially when mixed with plant residues or combined with mild thermal activation—has resulted in significant increases in biomass and improved soil fertility indicators (Pereira *et al.,* 2021; Rani *et al.,* 2022; Said *et al.,* 2018). For legumes (common bean and Centrosema), the mineral led to higher tissue K concentrations, better green biomass, and a balanced nutritional status, showing its potential to partially replace traditional K fertilizers (Barłóg *et al.,* 2022).

Studies on horticultural crops, such as lettuce and tomatoes, have demonstrated promising results when phlogopite is combined with mineral-enriched biochar, resulting in improved water-use efficiency and enhanced nutrient retention in the soil (Buss *et al.,* 2022). Controlled-release formulations—especially those that include phlogopite in remineralizer matrices—have promoted better growth of Mimosa scabrella seedlings and increased root vigor (Gabira *et al.,* 2022).

Notably, these results demonstrate that the agricultural potential of phlogopite is heavily dependent on its activation method and cropping system. While ground phlogopite offers a slow, steady K release suitable for long-term soil remineralization, bioactivated or thermally treated variants can provide intermediate nutrient-release rates ideal for modern cropping systems focused on sustainability and circular nutrient management (Basak *et al.,* 2022; Cordeiro, 2024).

7. ECONOMIC AND ENVIRONMENTAL ASPECTS

Replacing imported potassium chloride (KCl) with alternative K-bearing minerals such as phlogopite, biotite, and K-feldspar offers both economic and environmental benefits, especially for emerging agricultural economies like Brazil and India. High logistical, energy, and exchange-rate costs have historically increased fertilizer prices, making local mineral substitutes more competitive (Basak *et al.,* 2021; Swoboda *et al.,* 2022; Pereira *et al.,* 2021).

From an economic perspective, using low-grade potassium silicates or mining by-products can lower K input costs by 25–35%, especially when combined with regional grinding and blending facilities integrated into existing mining operations (Pereira *et al.,* 2021; Ciceri *et al.,* 2019). However, these savings are partly offset by the energy required for comminution, thermal activation, and acid or hydrothermal treatments, which involve capital expenditure (CAPEX) for dedicated processing infrastructure and operational costs (OPEX) related to energy and reagent use (Said *et al.,* 2018; Basak *et al.,* 2022).

From an environmental point of view, replacing imported KCl with local minerals helps reduce carbon emissions from maritime transport, decreases pressure on limited sylvinite deposits, and adds value to mine tailings and ultramafic residues (Buss *et al.,* 2022; Cordeiro 2024). However, the sustainability benefits rely heavily on the chosen activation method: mechanochemical and biological activation have low environmental impacts, whereas acid and thermal methods can produce acidic effluents, NO_x/SO_x gases, and significant CO_2 emissions (Said *et al.,* 2018). Consequently, lifecycle assessments should consider energy efficiency, effluent management, and waste valorization to ensure compatibility with circular economy principles (Smol, 2021; Tanguler-Bayramtan *et al.,* 2024).

Integrative feasibility analyses should jointly assess raw material availability, regional logistics, processing scalability, and public incentives for rock powder remineralizers—a regulatory trend already developing in Brazil and India (Basak *et al.,* 2021; Grams; Rehwaldt, 2025).

Table 7 provides aggregated estimates of phlogopite reserves in Brazil and worldwide. However, it is important to note that because phlogopite is often a byproduct or inert component associated with the mining of other commodities (such as gemstones, feldspars, and pegmatites), it rarely has formally measured and reported mineral resources based on detailed geological assessments. Therefore, the figures presented are approximations that may diverge significantly from actual volumes.

Table 7. Estimated Phlogopite Reserves in Brazil and Worldwide. Adapted from: Basak *et al.* (2021, 2022); Buss *et al.* (2022); Ciceri *et al.* (2019); Cordeiro (2024); Grams & Rehwaldt (2025); Pereira *et al.* (2021); Said *et al.* (2018); Smol (2021); Swoboda *et al.* (2022); Tanguler-Bayramtan *et al*. (2024); USGS (2025)

Region / Country	Main Sources	Annual Production (t)	Official Reserves (USGS 2025)	Estimated Geological Resource Scale ‡
Brazil	Pegmatites & ultramafic tailings (Bahia, Minas Gerais)	n/a	Not officially reported	≥ 5 million t (mostly in tailings)
India	Pegmatite-hosted deposits & mica-rich mines	14,000 – 15,000	~1,000 t	Multiple millions of tons
Russia	Ilmen Ural & Karelia pegmatites / ultramafics	n/a	Not disclosed separately	≥ 10 million t (likely)
Canada	Lac La Motte (Quebec – Ontario region)	~15,000	Large (unspecified)	Several million t
China	Multiple provinces – industrial mica mining	~80,000	~1.1 million t (sheet mica)	Tens of millions t regionally
South Africa	Limpopo ultramafic complexes	n/a	Not specified	≥ 1 million t (probable)

Available evidence suggests that phlogopite reserves are significantly underestimated, especially in Brazil, where large quantities remain stored in tailings from pegmatite and ultramafic operations without mineral resource certification (Basak *et al.,* 2021). These unquantified stocks represent a latent strategic asset for both fertilizer self-sufficiency and the valorization of industrial by products.

To turn this geological potential into practical agronomic use, systematic characterization and beneficiation studies are necessary, including mineralogical mapping, grinding energy assessments, and solubility profiling under sustainable processing methods. Public-private partnerships and policy tools that identify remineralizers as official fertilizer categories could help develop a domestic K supply chain, reducing reliance on imports and promoting regional circular economies (Cordeiro, 2024; Smol, 2021; Grams; Rehwaldt, 2025).

Figure 11 shows the estimated cost per nutrient unit (USD per kg K_2O) for three potassium sources: natural phlogopite (~0.35 USD/kg K_2O), activated phlogopite (~0.55 USD/kg K_2O), and imported potassium chloride (KCl, ~0.80 USD/kg K_2O).

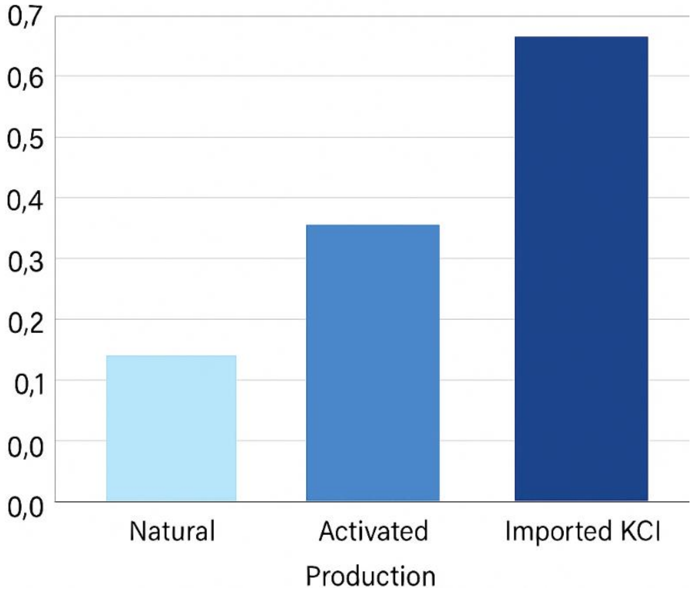


Figure 11. Comparative Economic Potential of Potassium Sources. Adaptado de Basak *et al.* (2021); Pereira *et al.* (2021); Swoboda *et al.* (2022); Said *et al.* (2018); Lodi *et al.* (2021); Buss *et al.* (2022)

The results show that natural and locally sourced phlogopite deposits can provide a significant economic benefit—up to 56% lower nutrient costs compared to imported KCl. Even after mechanical or thermal activation, phlogopite remains cost-effective, mainly because processing costs are balanced by reduced logistics and foreign exchange reliance (Basak *et al.,* 2021; Pereira *et al.,* 2021; Swoboda *et al.,* 2022).

From a strategic perspective, this comparison highlights the potential for import substitution in potassium-dependent economies, such as Brazil and India, where over 90% of potassium fertilizers are currently imported. However, the apparent cost advantage of phlogopite-based sources should be viewed with caution. Unlike KCl, which offers immediate solubility, phlogopite releases potassium gradually, necessitating medium- to long-term agronomic validation to assess its residual impact on soil fertility (Said *et al.,* 2018; Lodi *et al.,* 2021).

In environmental terms, the local exploitation of potassium-rich micas can decrease the carbon footprint associated with long-distance fertilizer transportation and support the circular use of mining by-products (Buss *et al.,* 2022). However, large-scale beneficiation or activation of phlogopite must address the energy and effluent management issues associated with thermal and acid processes.

8. CONCLUSIONS

Phlogopite has significant potential as an alternative, sustainable source of potassium, especially in regions heavily dependent on imported fertilizers, such as Brazil and India.

Its natural abundance in ultramafic and pegmatitic environments, along with advances in activation technologies—mechanochemical, hydrothermal, and thermochemical—has enabled the extraction of agronomically relevant amounts of potassium under controlled conditions. Experimental and field studies consistently demonstrate improvements in crop yield, soil nutrient balance, and water-use efficiency, confirming its suitability as a slow-release and residual fertilizer.

However, technical and economic limitations still restrict its large-scale use. The mineral's naturally low solubility and high energy needs for activation (such as grinding or calcination) raise operational costs and environmental impacts. Additionally, geological reserve data remain incomplete because phlogopite is usually considered a secondary or accessory mineral in mining operations and is therefore underreported in official databases. This uncertainty hampers accurate feasibility studies and policy planning.

Looking ahead, future research and innovation should focus on:

- Energy-efficient activation pathways, such as mild thermal or bio-assisted treatments.
- Long-term soil monitoring, evaluating nutrient cycling, microbial dynamics, and secondary mineral formation.
- Integrating the circular economy by valorizing mining residues and linking them with carbon sequestration or waste management efforts.
- Regulatory and policy frameworks that promote the certification and commercialization of remineralizers made from phlogopite and related micas.

In conclusion, the agronomic use of phlogopite offers a practical path toward diverse, low-carbon, and regionally resilient potassium supply chains. When combined with sustainable processing and supportive policy measures, this approach can help close the gap between resource availability and fertilizer security, promoting both soil regeneration and agro-industrial sustainability.

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