

Vermiculite: Nature's Versatile Mineral

K.N Prakash Narasimha,

Former Professor, Dept. of Earth Science,
Centre for Advanced study in Precambrian Geology,
University of Mysore, Mysore-570 006.

Vishwanath. R,

Guest faculty, Dept. of Applied Geology,
Kuvempu University, Shivamogga-577451.

Abstract: Vermiculite, a hydrated silicate mineral derived from the alteration of biotite or phlogopite mica, is characterized by its unique layered structure and ability to expand when heated. This paper provides a comprehensive overview of vermiculite, exploring its mineralogical properties, geological occurrences, formation processes, and industrial applications. The study examines the three main types of vermiculite-bearing ultramafic-mafic intrusives and highlights significant global and Indian deposits. Particular attention is given to the vermiculite occurrences in the Western and Eastern Dharwar Cratons of southern India, noting the differences in host rocks, mineral composition, and alteration sequences. The paper also discusses the wide-ranging industrial applications of exfoliated vermiculite, from construction and agriculture to environmental remediation. Recent research on vermiculite's adsorptive and chemical reactive properties is presented, emphasizing its potential in addressing environmental challenges. This comprehensive review provides valuable insights into the mineralogy, geology, and economic importance of vermiculite, serving as a reference for researchers, industry professionals, and policymakers involved in the study and utilization of this versatile mineral.

Key words vermiculite, mineralogical properties, Industrial applications

Prologue

The name of Vermiculite is derived from the Latin word "vermiculare" (meaning "to breed worms"), is a platy mineral closely related to biotite. It is a hydrated silicate with the general formula: $(\text{Mg}, \text{Ca})_{0.7} (\text{Mg}, \text{Fe}^{3+}, \text{Al})_{6.0} [(\text{Al}, \text{Si})_8 \text{O}_{20}] (\text{OH})_4 \cdot 8\text{H}_2\text{O}$. The term "hydrate" refers to the structural water located between the silicate layers. Besides this structural water, vermiculite also contains non-structural water, which varies based on its porosity and the relative humidity. On a molecular level, vermiculite consists of two tetrahedral silicate sheets facing each other, joined by an octahedral sheet containing aluminum and iron. This arrangement forms the basic structure of a single biotite layer. Mica flakes are created by stacking these layers in repetition. Each unit layer has regularly spaced "holes" on its upper and lower surfaces, which align with corresponding sites on adjacent layers (Grim, 1953, 1962). In biotite, potassium atoms fill these sites, and their electronic charges help bind the layers together. In vermiculite, however, only some of these sites are typically occupied by magnesium, and water molecules form a double layer in these interlayer spaces. When heated, the water turns to steam, causing the vermiculite to expand. Vermiculite is a secondary mineral, resulting from the alteration of biotite, phlogopite mica, or chlorite (Bush, 1976; de la Calle and Suquet, 1988). Phlogopite and biotite belong to a solid solution series of potassium magnesium iron aluminum silicate hydroxides, ranging from magnesium-rich phlogopite to iron-rich biotite.

Occurrence of Vermiculite

(i) Macroscopic Vermiculite

Macroscopic vermiculite is characterized by its high magnesia and water content, but it contains low amounts of iron oxide and potash. These properties are thought to be inherited from the original biotite or phlogopite, making it true vermiculite. During the alteration of biotite or phlogopite into vermiculite, ferrous iron is converted to ferric iron. Macroscopic vermiculite is typically brown with a bronzy luster. Those derived from

phlogopite are yellow to yellowish- brown, while those formed from biotite are black, brownish-black, or green. When heated rapidly to 1100°C, vermiculite expands accordion-like due to the conversion of its water content into steam, resulting in elongated, worm-like, lightweight particles. The degree of expansion can range from 6 to 30 times its original thickness, with lower expansion attributed to interlayering of vermiculite with 1:1 biotite-vermiculite (hydrobiotite), while higher expansion suggests pure vermiculite (Bush, 1976). In addition to vermiculite, mixed-layer mica/vermiculite is a common mineral derived from mica. These mixed-layer minerals consist of interstratified mica and vermiculite, with variable amounts of each component arranged either randomly or in a regular sequence. When biotite and vermiculite are regularly interstratified, the mineral is known as hydrobiotite. The formation of macroscopic vermiculite is attributed to weathering, alteration by groundwater, and low-grade metamorphic processes. Industrial-grade vermiculite deposits are believed to result from the weathering and groundwater alteration of macroscopic biotite mica, iron-bearing phlogopite, or chlorite (Basset, 1961; Libby, 1975; Hindman, 1994; Frank and Edmond, 2001).

(ii) Vermiculite Clays

Vermiculite clays, derived from a diverse range of parent materials, occur in two distinct types. The first is an aluminous type, where Al^{3+} is the dominant ion in the octahedral layer. In this Type, Al^{3+} replaces Si^{4+} in the tetrahedral positions, similar to what occurs in coarse-grained or macroscopic vermiculites. The second type is siliceous, with Fe^{3+} and Mg^{2+} as the primary octahedral ions, and only Si^{4+} occupying the tetrahedral positions. The aluminous variety is typically found in soils derived from acid igneous rocks and is usually associated with mica, while the siliceous variety is found in soils originating from basic igneous rocks, which lack mica. Given the strong connection between these vermiculites clay types and their parent materials, the aluminous type is considered a product of mica alteration, whereas the siliceous type forms through synthesis from primary oxides of silica, alumina, iron, and magnesium. Both types of vermiculite clays tend to be dioctahedral, unlike the trioctahedral structure of coarse- grained macroscopic vermiculite (Barshad and Kishk, 1969).

Geological environment of Vermiculite occurrence

Vermiculite is found in various geological settings, (a)Soils over sedimentary and metamorphic rocks (b)Deep-marine sediments (hot-brine deposits) linked to submarine hydrothermal activity (c)Ultramafic/mafic rocks (d)Volcanoclastic tuffs (e)Metamorphic rocks.

(a)Soil Vermiculite

Soils formed over sedimentary and metamorphic rocks often contain chlorites, which weather into vermiculite. This occurs through the selective removal of alternate hydroxide (brucite) layers in the chlorite lattice, which are replaced by exchangeable cations and water.

(b) Vermiculite in deep-marine sediments

At the Atlantis II Deep in the Red Sea, hydrothermal marine vermiculite is found in hot- brine deposits, associated with authigenic clays. This vermiculite likely originates from basic volcanic ejecta, forming through precipitation from solutions supersaturated with silicon, magnesium, and iron. The necessary magnesium is believed to come from the halmyrolitic decomposition of basic volcanic ejecta (Singer and Stoffers, 1981).

(c) Vermiculite in Ultramafic/Mafic Igneous rocks

Commercial vermiculite deposits occur in ultrabasic to basic-acidic/alkalic intrusive environments. In these rocks, vermiculite forms as a secondary mineral through weathering (supergene alteration) of precursor minerals like biotite, ferruginous phlogopite, and chlorite. These precursor minerals result from the hydrothermal alteration of olivine or minerals from the pyroxene and amphibole groups.

(d) Vermiculite in volcanoclastic tuffs

Studies by Melka et al. (2000) on the tuffs in the Doupovské Hory mountains in the Czech Republic revealed the presence of hydrobiotite, phlogopite, smectite, and vermiculite within mica flakes. This suggests that the mica plates in the tuffaceous material consist of regular interstructural alternation between biotite/phlogopite and vermiculite. The alteration of phlogopite due to weathering has led to the formation of mixed-layer phlogopite and vermiculite (hydrophlogopite).

(e) Vermiculite of metamorphic origin

Vermiculite has also been reported to form through low-grade metamorphism of pelitic sedimentary rocks and mafic/acidic igneous rocks (Velde, 1978; Ruiz Cruz, 1999; Ruiz Cruz and Rodriguez Jimenez, 2002; Ruiz Cruz

and Novak, 2003). Velde (1978) studied metamorphic vermiculites in pelitic rocks, showing that they form from chlorite in a sequence: chlorite → chlorite/vermiculite mixed layers vermiculite. According to Velde, metamorphic vermiculite is sensitive to pressure and temperature, crystallizing near the upper limits of the muscovite- chlorite assemblage below biotite-bearing facies.

Classification of Vermiculite-bearing Ultramafic and Mafic rocks

Unlike metalliferous deposits, vermiculite deposits exhibit relatively petite variation in their geological settings and formation processes. For instance, copper deposits occur in a wide range of geological environments and are formed through various genetic processes, such as magmatic, hydrothermal, volcanogenic, and sedimentary mechanisms. In contrast, vermiculite deposits do not display such diversity in either their geological environments or their modes of origin. As a result, there is no established genetic classification of vermiculite deposits in geological literature. However, vermiculite-bearing ultramafic and mafic bodies do exhibit some differences in their geological settings. According to Bush (1976), vermiculite-bearing host rocks can be grouped into three types; Type 1, Type 2, and Type 3 though all three types share notable similarities.

A brief overview of the geological settings for Type 1, Type 2, and Type 3 vermiculite- bearing ultramafic-mafic intrusive, along with representative examples of vermiculite deposits associated with each type, is addressed.

Type 1 Vermiculite-Bearing Ultramafic-Mafic Intrusives

Type 1 intrusives consist of large ultramafic bodies, such as zoned pyroxenite or carbonatite plutons, often intersected by syenites or alkalic granites. Typical examples of these intrusives include the Vermiculite-bearing ultramafic bodies at Palabora in South Africa and Libby in Montana, U.S.A., as cited by Bush (1976). Additionally, Van Gosen et al. (2002) identified three more examples of smaller vermiculite-bearing intrusives: the Gem Park Complex and Iron Hill Carbonatite Complex, both located in Colorado, U.S.A., and the Gold Hill Stock in Idaho, U.S.A. The Kovdor alkaline igneous and carbonatite complex on the Kola Peninsula in Russia is also classified within this type.

Type 2 Vermiculite-Bearing Ultramafic-Mafic Intrusives

Type 2 intrusives consist of small to medium-sized ultramafic bodies, such as dunite, unzone pyroxenites, and peridotites, often intersected by pegmatites, syenites, or granites. Notable examples include the vermiculite-bearing serpentinite in the Blue Ridge region of North Carolina (known as the Day Book dunite) and the Smith Mine in Wyoming, U.S.A., as identified by Bush (1976) and Van Gosen (2002). A review of the geological literature suggests that several other vermiculite-bearing ultramafic bodies around the world can also be categorized as Type 2 intrusives.

Type 3 Vermiculite- Bearing Ultramafic-Mafic Rocks

Type 3 vermiculite-bearing intrusives consist of metamorphosed ultramafic-mafic rocks, such as biotite schist, amphibolite schist, and mica-amphibole schist, which are occasionally intersected by or in contact with pyroxenites, peridotites, and pegmatites. An example of this type includes the vermiculite-bearing mafic schists of the Enoree district, particularly in Tigerville, South Carolina, U.S.A. (Bush, 1976). Globally, Type 3 ultramafic-mafic rocks are commonly found in Precambrian metamorphic terrains and ophiolite zones. Additional examples include the Askos vermiculite-bearing ultramafic rocks in Macedonia, Greece, and vermiculite- bearing amphibolite's in the Precambrian schistose rocks of Palamau district, Bihar, India.

Significant Global and Indian Deposits of Vermiculite

Geological features and genesis of vermiculite deposits have been documented in various global locations, including Nagasaki Prefecture in Japan (Nakamuta, 1981), the Malaguide Complex in Spain (Ruiz Cruz and Novak, 2003), Hafafit in Egypt (El Shazly et al., 1975), Central Turkey (Toksoy-Koksal et al., 2001), Askos in Macedonia, Greece (Tsirambides and Michailidis, 1999), and numerous regions across the United States (Bassett, 1959; Bush, 1976; Van Gosen et al., 2002). Presently, significant vermiculite production occurs in South Africa, China, Brazil, Zimbabwe, and the United States. Major operational mines are situated in the Palabora region of northeastern Transvaal, South Africa; in northwestern China; and along the eastern Appalachian range in Virginia and South Carolina, USA. The vermiculite ores extracted from these sites predominantly consist of various forms of hydrated phlogopite or biotite mica, which possess the unique ability

to exfoliate. In most of the regions mentioned, vermiculite has been observed to form at the contact zones between ultramafic rocks and acid igneous intrusives (Goldstein, 1946; Bush, 1972). In Africa, vermiculite deposits have been identified in the Republic of South Africa (Gevers, 1949) and Tanganyika (Williams and Skirl, 1940). The largest known deposit is located in the Loolekop area of the Palabora district in North Transvaal, where it is found within pyroxenite and serpentines rock, covering an area of six to seven square miles (Gevers, 1949). In the United States, vermiculite has been reported from eleven localities, with production centered in seven areas. The largest deposit is in Libby, located in the Rainy Creek district of Lincoln County, Montana. Commercial-grade vermiculite deposits are also noted in Colorado, Wyoming, North Carolina, and Georgia, with additional occurrences in Arizona, South Carolina, Pennsylvania, Nevada, Maryland, Oregon, Texas, Utah, and Massachusetts. Despite the recognition of these deposits, production from states other than Montana and North Carolina has been limited and sporadic (Goldstein, 1946). In Russia, vermiculite deposits have been found in the Ural Mountains, associated with dunite and pyroxenite intrusives (Kazantsev, 1934). In Australia, significant vermiculite deposits are primarily located in the Young River area of Western Australia, with several new discoveries currently under development. In Greece, extensive metasomatic zones of vermiculite, tremolite, chlorite, and talc-rich rocks have been documented at the contact zones between serpentinitized ultramafic bodies and surrounding two-mica gneisses in the Askos region of Macedonia (Tsirambides and Michailidis, 1999). In Brazil, the largest deposit is situated in the Catalao/Ouvidor region of Goiás state in central Brazil, while the Paulistana region in Piauí, Northeast Brazil, hosts the second-largest occurrence. These vermiculite deposits are associated with ultramafic intrusives found within country rocks composed of garnet schists and Lower Proterozoic age migmatites. Occurrences of vermiculite have been documented in several Indian states, including Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Tamil Nadu, Karnataka, Rajasthan, and West Bengal. These states have intermittently produced vermiculite. While vermiculite deposits have been noted in various regions of the Indian subcontinent, only a limited number have been studied in detail. In Bihar, a significant deposit is located in the Biwabathan area of Palamau district, found at the contact zones of altered amphibolite and biotite-gneiss, near granitic and pegmatitic bodies (Chattopadhyay and Bhattacharyay, 1994). Additional mineralization has been reported in parts of Bhagalpur district, also in Bihar (Chattopadhyay and Sengupta, 1991). Furthermore, Prasad and Majumdar (1966) identified hydrobiotite occurrences in Bhagalpur and Santhal Parganas districts. The vermiculite deposits in these Bihar locations are believed to have formed through a combination of hydrothermal and supergene weathering processes. In Karnataka, vermiculite occurrences have been recorded in various areas, including Harohalli in Mandya district, Talur, Gopalpura, Thoravalli, and Chunchunkatte in Mysore district, as well as Malavanaghatta, Jadukata, and Bageshpura in Hassan district. Additionally, occurrences have been noted at Kamasamuddram and Pavagada in Kolar district and Nidavanda, Nandihalli, Billenahalli, and Mahadevarahalli in Shimoga district (Radhakrishna, 1948; Ramamurthy, 1960). In many of these locations, vermiculite appears as narrow bands at the margins of altered ultramafic rocks in contact with acidic intrusions. However, detailed information regarding the field settings, host rock petrography, types of younger intrusions, and the genesis of these vermiculite occurrences remains scarce. Recently, Prakash Narasimha et al. (2004; 2006a, 2006b, 2009, 2011, 2012, 2015, 2016) reported on the geological features and genesis of vermiculite occurrences in the western and eastern Dharwar cratons.

Western Dharwar Craton

Sargur schist belt: Vermiculite occurs in Gopalpura, Agasthyapura, Hadanahalli, Kalbetta, Harohalli , Thoravalli, Talur etc..

Nuggihalli schist belt: Malavanaghatta, Ponnasamudra and Belagumba

Eastern Dharwar Craton

Kolar schist belt:(Sakarsanahalli association): Ajjampalli, Kamasamudra and Dodda betta

Differences between the Vermiculite mineralization of Eastern and Western Dharwar Craton.

The Dharwar craton in southern India, comprising the Western Dharwar Craton (WDC) and Eastern Dharwar Craton (EDC), exhibits significant differences in litho-types, geochronology, structure, and metamorphism. Notably, there are also observable differences in vermiculite mineralization between the eastern and western

sections of the craton. The presence and genesis of vermiculite in the Western Dharwar Craton have been documented by Radhakrishna (1948), Ramamurthy (1960), and Prakash Narasimha et al. (2004; 2006a, 2006b). In comparison with the current study on the vermiculites of the Eastern Dharwar Craton, several differences emerge, including: Both the western and eastern Dharwar cratons contain vermiculites associated with the Type-3 ultramafic-mafic rocks described by Bush (1976), though the host rocks differ. In the western Dharwar craton, the host rocks are primarily composed of meta pyroxenites, with some instances of metagabbro. Conversely, in the eastern Dharwar craton, the host rock for the studied vermiculite occurrences is amphibolite. The 'vermiculite ore' in the western Dharwar craton consists of vermiculite and hydrobiotite, with some areas containing only hydrobiotite. In contrast, the 'vermiculite ore' in the eastern Dharwar craton comprises interstratified grains of vermiculite and hydrobiotite, and no occurrences of hydrobiotite alone have been reported there. The sequences of mineral alteration leading to vermiculite formation differ between the eastern and western Dharwar cratons. In the western Dharwar craton, the sequence of alteration is as follows: Ortho/Clinopyroxene (primary) → Hornblende/Biotite (secondary) → Hydrobiotite (intermediate stage) → Vermiculite (tertiary stage). In the eastern Dharwar craton, vermiculite formation occurs in this sequence: Hornblende (primary) → Biotite (secondary) → Hydrobiotite (intermediate stage) → Vermiculite (tertiary stage).

Uses of Vermiculite

Exfoliated vermiculite serves a wide range of industrial applications. In its raw form, vermiculite has limited utility. However, it is chemically stable, showing no reaction to weak inorganic acids, bases, or organic solvents. With a high cation-exchange capacity, it is relatively refractory and has low thermal, electrical, and acoustic conductivity. These characteristics contribute to its versatility, making it ideal for various uses, including lightweight concrete and plaster for roof decks, curtain walls, and acoustical and fire-retardant applications. Vermiculite is commonly used for loose-fill insulation in hollow masonry walls and double-walled cryogenic tanks, as well as for insulating hot ingots and molten-metal ladles. In loose form, it also serves as a packing material for corrosive or reactive substances. Finely ground vermiculite is utilized as an extender, filler, or pigment in paints, enamels, rubber, plastics, inks, and lubricants. In agriculture, it acts as a carrier for pesticides and fertilizers, an absorbent for dry additives, a soil conditioner, and a component in feed for chickens, swine, dogs, and livestock. Additionally, vermiculite is employed as a dust suppressant in underground mining and as a filter for radon daughter products in uranium mining. Recent mineralogical studies on vermiculite have examined its adsorptive and chemical reactive properties, which are particularly significant in environmental applications involving gas and liquid absorption or heterogeneous catalysis processes. Its interlayer adsorption capabilities make vermiculite effective in collecting organic toxins. By manipulating the chemistry and interlayer charges of vermiculite using specific solutions, its adsorption properties can be enhanced or controlled. Ultimately, chemically modified vermiculite may play a role in the remediation of toxic spills or contaminated sites and is also useful in nuclear waste disposal. Furthermore, vermiculite's presence in soils can influence the mobility of potassium and other elements, impacting soil management practices. Interestingly, vermiculite finds applications in unconventional areas as well. For instance, in commercial bread baking, water-saturated vermiculite is applied to the first row of bread pans before they enter the oven to absorb the flash heat that scorches the first loaves. While the water is not reclaimable, the vermiculite can be reused.

Conclusions

This comprehensive review of vermiculite mineralogy, geology, and industrial applications highlights the complexity and importance of this unique mineral. Several key points emerge from this study: Vermiculite, a hydrated phyllosilicate mineral, occurs in various geological settings, including soils, marine sediments, ultramafic/mafic rocks, volcanoclastic tuffs, and metamorphic rocks. Its formation is primarily attributed to the alteration of biotite, phlogopite, or chlorite through weathering, hydrothermal processes, or low-grade metamorphism. The classification of vermiculite-bearing ultramafic and mafic rocks into three types (Type 1, Type 2, and Type 3) provides a framework for understanding the diverse geological contexts in which vermiculite occurs globally. Significant differences in vermiculite mineralization have been observed between the Eastern and Western Dharwar Cratons in India, reflecting the complex geological history of the region and the varied processes of vermiculite formation. The industrial applications of vermiculite are diverse and wide-

ranging, from construction and agriculture to environmental remediation and nuclear waste disposal. Its unique properties, including low density, high cation-exchange capacity, and thermal insulation, make it a valuable material in numerous sectors. Recent research has focused on the adsorptive and chemical reactive properties of vermiculite, opening new avenues for its application in environmental cleanup and contamination control.

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