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Exploring Greenockite: Occurrences and Geological Setting

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Abstract:
Greenockite, mineral containing cadmium, is of significant scientific interest owing to its remarkable properties and potential applications in the field of science. It commonly forms in hydrothermal ore deposits as a secondary mineral due to complex cadmium-sulfur interactions influenced by temperature. Typically, it replaces zinc minerals like sphalerite, depending on the abundance of cadmium and zinc in hydrothermal fluids. Solid solubility in the ZnS-CdS system occurs at high temperatures, with immiscibility observed under specific conditions. Greenockite forms at relatively low temperatures (100°C to 200°C) and is influenced by factors such as oxygen fugacity, hydrogen sulfide activity, and chloride ion content. Its hexagonal zinc blende structure results in diverse crystal forms, including rods, wires, and whiskers, often adorned with bismuth drops. Experimental studies have identified factors affecting its formation, such as solid solubility, precipitation mechanisms, pH levels, and fluid composition. Its vibrant coloration, attributed to cadmium concentration, varies from pale yellow to deep orange-red. Geologically, it is present in diverse settings, including metamorphosed zinc oxide mineralization, granites, fumaroles, pegmatites, and sediment-hosted Pb-Zn deposits, with a unique occurrence in gabbroic rock at the Babbitt deposit. In India, Greenockite has been identified in the Bagada orogenic gold prospect, situated within the Paleoproterozoic Mahakoshal belt, Central Indian Tectonic Zone (CITZ). Additionally, it is found in hydrothermal deposits of Pb-Zn mines of Zawar. It is exclusively encountered within specific geological settings, primarily as a secondary product. This paper provides a comprehensive exploration of its geological occurrences, distribution, associations, and exceptions.

Keywords: *Cadmium, Greenockite, Geochemistry, Cadmium-Sulfur Interactions, Geological Settings*

INTRODUCTION TO GREENOCKITE

Cadmium, an abundant transition metal in the Earth's crust, is renowned for its versatile properties and wide-ranging applications across various industrial and technological domains (Nriagu, 1983; Jarup, 2003). Its presence in the natural environment holds profound implications for both the scientific community and society. Greenockite, scientifically known as cadmium sulfide (CdS), plays a pivotal role as the representative mineral of cadmium ore. This mineral displays vibrant yellow to orange-red pigmentation, semiconductor attributes, and intriguing connections to environmental and health considerations (RankamaandSahama, 1950; Schwartz, 2000). Greenockite, captivating scientists and mineralogists for centuries, occupies a prominent position within the scientific community. Its journey to recognition commenced in the early 19th century with its discovery in the Scottish town of Greenock. The distinct characteristics of Greenockite have garnered significant attention.

The significance of studying Greenockite's distribution and geochemistry lies in its multifaceted contributions to various scientific disciplines and societal concerns. An exploration of Greenockite's distribution and geochemistry unveils insights into Earth's history, as its occurrence in diverse geological settings offers clues about the conditions and processes that shaped these formations (Rankama and Sahama, 1950). Greenockite's presence often serves as an indicator of valuable ore deposits, providing essential information for resource prospecting and mining. Greenockite's geochemical behavior holds significant potential in the realm of materials science, particularly in the development of renewable energy technologies such as solar cells. Its semiconducting properties render it a valuable component in various technological applications, driving innovations in electronics and optoelectronics (Schwartz, 2000). Cadmium's significance spans industry, technology, environmental considerations, regulatory measures, and ongoing research and innovation. It exemplifies the intricate balance required to harness the benefits of elements with potential risks, underscoring the importance of scientific research and responsible practices in managing such materials. Greenockite historically utilized as a pigment in ceramics and paints, as noted in a study by Nassau (1983) on the history of cadmium pigments. Its semiconducting properties have also been explored, with cadmium sulfide being employed in the production of photovoltaic cells, as discussed in a paper by Wang et al. (2018) on cadmium-based solar cells. However, these applications have waned due to concerns regarding cadmium's toxicity and the development of safer, more efficient materials. In recent times, greenockite's significance has shifted towards its role as a reference material in laboratory research, particularly in crystallography and mineralogy studieson cadmium minerals. The use of greenockite remains limited, with safety and environmental regulations surrounding cadmium-containing materials a significant consideration (Kossoff et al., 2014).Cadmium sulfide exhibits remarkable versatility in various applications. Notably, it plays a crucial role in the production of solar cells, serving as a vital buffer layer in the manufacture of CIGS (Copper-Indium-Gallium-Selenide) solar cells (AZoM, n.d.). Given the surging interest in and adoption of solar cell technology, there is a strong likelihood that the demand for cadmium sulfide in this application will significantly increase in the future. Furthermore, cadmium sulfide finds utility in a diverse range of applications, including its use in light-dependent resistors or photoresistors for light sensors, chemical bath deposition (CBD), sol-gel techniques, metal-organic chemical vapor deposition (MOCVD), sputtering, electrochemical deposition, and even in processes like spraying with precursor cadmium salt, sulfur compounds, and dopants, as well as screen printing using a slurry containing dispersed CdS(AZoM, n.d.). These multifaceted applications underscore the adaptability and significance of cadmium sulfide in various technological and scientific processes. While historically known for its use as a pigment, the future is poised to witness an expanding role for cadmium sulfide, particularly in the flourishing solar cell market, driven by the increasing acceptance and affordability of solar cell technology (AZoM, n.d.).

This comprehensive review delves deeply into the captivating world of Greenockite, exploring its physical and optical properties, crystallographic characteristics, genesis, geochemistry, and diverse deposits. The paper consolidates all available data related to the geological importance of Greenockite, addressing a crucial knowledge gap as no combined dataset of Greenockite occurrences currently exists. This endeavor aims to reveal the historical context and geological implications of Greenockite's presence in diverse geological settings, building upon the foundational work of

Rankama and Sahama in 1950. Thus, this paper serves as a unique and invaluable resource for gaining a deeper understanding of the multifaceted significance of Greenockite and cadmium, a pursuit that remains ongoing in the present day.

GENESIS OF GREENOCKITE

Greenockite, with the chemical formula CdS, is a cadmium sulfide mineral that forms under specific geological conditions. Its creation is closely linked to the development of hydrothermal ore deposits, which occur when mineral-rich fluids permeate fractures in the Earth's crust. Typically, Greenockite emerges as a secondary mineral within these deposits, crystallizing after primary minerals have already formed. The process of Greenockite formation primarily hinges on the presence of cadmium (Cd) and sulfur (S) in these hydrothermal fluids. Cadmium is often associated with zinc (Zn) minerals, and Greenockite can replace zinc minerals like sphalerite (ZnS). The formation process involves the combination of cadmium ions and sulfur ions within the hydrothermal solution, leading to the creation of Greenockite crystals. The specific conditions required for Greenockite formation encompass the availability of cadmium-rich fluids and suitable temperature conditions.

Greenockite, a mineral forged through a complex interplay of geological processes, is known to manifest in diverse geological settings, each with its unique set of conditions and histories. Among these settings are metamorphosed zinc oxide mineralization, granites, fumaroles, pegmatites, hydrothermal ore deposits, and sediment-hosted Pb-Zn deposits. The mineral's propensity to materialize across such a spectrum of geological environments attests to the intricate interplay of geological factors influencing its formation (Johnson et al., 1990; Butler and Thompson, 1967a; Chaplygin et al., 2007; Černý and Harris, 1978; Oen et al., 1974; Tarkian and Breskovska, 1989; Tombros et al., 2005; Patterson, 1985; Li et al., 2018). Remarkably, Greenockite is commonly linked with felsic rock types in magmatic environments, with an exception found in the gabbroic rock of the Babbitt deposit in the Duluth Complex, Northeastern Minnesota (Hauck and Severson, 2000a). This unique occurrence defies convention, as Greenockite is often present in minor quantities within sphalerite, with cadmium concentrations rarely exceeding 50,000ppm. As sphalerite undergoes weathering, it commonly transforms into zinc carbonate, known as smithsonite, while the cadmium component precipitates as secondary Greenockite (Schwartz, 2000). This distinctive geological manifestation raises intriguing questions about the formation of Greenockite in such an environment.

Experimental studies have illuminated the conditions conducive to Greenockite formation. Solid solubility is observed between ZnS and CdS at temperatures exceeding 600°C, with narrow miscibility gaps noted at lower temperatures. Additionally, Greenockite formation appears to be influenced by various factors, including precipitation mechanisms, pH levels, fluid composition, and mineral-fluid equilibrium relationships. A recent discovery in the Baula-Nuasahi Complex revealed Greenockite in association with siderite-chlorite, challenging conventional wisdom as no original phases like sphalerite or shadlunite were observed. To explore potential cadmium sources, chalcopyrite samples were analyzed using LA-ICP-MS, shedding light on the enigmatic genesis of Greenockite in this specific geological context (Mishra and Hazarika, 2016).

The formation of Greenockite often involves the replacement of elements within geological formations. One of its most common replacement scenarios is the substitution of zinc minerals, particularly sphalerite (ZnS). This replacement process depends on several factors, including the relative abundance of cadmium and zinc in the hydrothermal solution and the thermodynamic stability of the minerals involved. When cadmium concentrations in the hydrothermal fluids are sufficiently high, they compete with zinc for available sulfur ions. If conditions favor the formation of cadmium sulfide (Greenockite) over zinc sulfide (sphalerite), Greenockite will precipitate and gradually replace sphalerite or other zinc minerals. This process can lead to the transformation of zinc-rich ores into cadmium-rich ones, which can have significant implications for mining operations and mineral resource management. The temperature at which Greenockite forms is a critical factor in its geochemistry. Greenockite typically forms in hydrothermal systems at relatively low temperatures compared to many other minerals in the same ore deposits. The specific temperature range for Greenockite formation can vary but often falls between 100°C and 200°C (212°F to 392°F). The relatively low formation temperature of Greenockite is a consequence of its thermodynamic stability under these conditions. At these temperatures, cadmium and sulfur ions in the hydrothermal solution combine to create the mineral structure of Greenockite. Higher temperatures would favor the formation of other cadmium minerals or phases, while lower temperatures may not provide the necessary energy for the crystallization of Greenockite (Mishra and Hazarika, 2016).

Greenockite is commonly found in association with a variety of minerals in hydrothermal ore deposits. These deposits often occur in specific geological settings, such as regions with volcanic activity, or near tectonic plate boundaries. The geological composition of rocks where Greenockite is found can vary widely, but several rock types are commonly associated with hydrothermal deposits. Hydrothermal fluids can migrate through and interact with sedimentary rocks, leading to mineral alterations and the formation of Greenockite. Examples of sedimentary rocks hosting Greenockite deposits include shale, limestone, and dolomite. Greenockite may also be found in metamorphic rocks that have undergone recrystallization due to heat and pressure. Examples include schist, marble, and gneiss. Some Greenockite deposits occur in association with igneous rocks, especially in areas with volcanic activity. These rocks can include granite, diorite, and basalt (Tombros et al., 2005).

GEOCHEMISTRY OF GREENOCKITE

The geology of Greenockite reveals the geological processes and conditions that have shaped its presence across various geological settings. Understanding its physical and optical properties and chemical composition is crucial. Greenockite's physical properties are primarily defined by its crystalline structure. This mineral crystallizes in the hexagonal crystal system, adopting the zinc blende structure, also known as the sphalerite structure. This arrangement is characterized by a cubic close-packed lattice of sulfur ions, with cadmium ions substituting some of the zinc sites (Cherin et al., 1970; Tauson and Chernyshev, 1977; Skinner and Bethke, 1961; Smith and Brown (2015), Mishra and Hazarika, 2016). Understanding this crystallography is fundamental to comprehending many of greenockite's characteristics.Greenockite's most distinctive feature is its remarkable coloration. It exhibits a vibrant spectrum of colors, ranging from pale yellow to deep orange-red. The intensity of the color is directly linked to the concentration of cadmium within the crystal lattice. This vivid pigmentation results from the specific arrangement of cadmium and sulfur ions, which interact with light to produce these striking hues. It typically falls within the translucent to transparent range on the transparency scale. Its transparency allows light to penetrate its crystal lattice to varying degrees. Regarding luster, it often displays a resinous or adamantine luster. This luster contributes to its visual appeal, giving Greenockite a glossy, attractive sheen when observed. In terms of hardness, Greenockite ranks relatively low on the Mohs scale, typically registering a hardness value of approximately 3. This relatively low hardness implies that Greenockite is relatively soft and can be susceptible to scratching and abrasion. Greenockite exhibits a characteristic cleavage, particularly along the {111} crystallographic planes. This cleavage is usually described as imperfect and can be observed when specimens are subjected to cleavage tests. In terms of fracture, Greenockite often showcases a conchoidal fracture, characterized by smooth, curved surfaces reminiscent of broken glass. This type of fracture results from the crystal's tendency to break along curved surfaces. Greenockite's optical properties are of particular interest due to its potential applications in optoelectronics and photovoltaics. Optical properties are defined by the refractive index, which typically ranges between 2.45 to 2.50, with variations depending on the wavelength of light and the crystallographic orientation (DeWild et al., 2007 and Chen et al., 2016). This mineral is classified as anisotropic, meaning it displays birefringence. When observed under a petrographic microscope, Greenockite can exhibit interference colors, a consequence of this birefringent behavior (DeWild et al., 2007). Greenockite also demonstrates dispersion, which refers to the separation of light into its constituent colors. When closely examined, Greenockite specimens may display a noticeable "fire" or play of colors, which is a result of this dispersion phenomenon. Each of these properties contributes to Greenockite's identity and potential applications, particularly in the realm of optoelectronics and the utilization of its unique optical behaviors.

Numerous empirical investigations have presented evidence supporting the existence of complete solid solubility within the ZnS-CdS system at elevated temperatures, particularly surpassing the threshold of 600°C. Nevertheless, it is important to highlight that under specific conditions, there is a noticeable immiscibility region. This immiscibility region becomes evident at various compositions. In contrast, Chaplygin et al. (2007) reported observations suggesting the precipitation of Cd-enriched zinc sulfides at relatively lower temperatures, roughly around 400°C. This contrasts with the formation of pure ZnS, which can take place at considerably higher temperatures, reaching up to 750°C, especially within fumarolic settings. Nonetheless, the replacement of Cd by Zn appears to be a multifaceted process, subject to various factors, including the precipitation mechanism, pH levels, oxygen fugacity (fO_2), hydrogen sulfide activity (H_2S), and conceivably, the chloride ion (Cl^-) content of the fluid. All these factors collectively influence the equilibrium relationships between minerals and fluids, as documented by Tauson and Chernyshev (1977), Wright and Gale (2004), and Tombros et al. (2005) in their respective studies.

An individual Greenockite crystal, measuring between 0.5 and 3 µm in size, exhibits the presence of prism faces {01-10}, pyramid faces {02-21}, and pedion faces {000-1}. Additionally, there are instances of Greenockite crystals displaying splitting in two distinct morphological forms: a sheaf-like configuration resulting from the cleavage of the {01-10} prism, and a "flower" type morphology stemming from the cleavage of (0001) or (000-1) faces, as documented by Novak et al. in 2020. Various morphological types, among which rods, wires, and whiskers with bismuth drops on crystal tops are predominant. Greenockite displays a variety of morphological forms, with rods being the most prevalent. These rods commonly grow outward from a single focal point, attaining a thickness of approximately 5–6µm and a length of roughly 10µm. The bismuth catalyst droplet situated atop these rods exhibits a diameter comparable to the rod's thickness (Novak et al. in 2020). Typically, the ratio of the rod's diameter to the droplet's diameter is less than 1.5. Smaller rods possess a rounded cross-section, whereas larger ones feature well-defined facets and tend to increase in thickness toward the catalyst droplet. These thicker rods elongate along specific crystallographic orientations, such as {01-10}, and showcase facets resembling pyramid faces {2-120}, as well as pedion faces {0001} and {000-1}. Greenockite also manifests in the form of whiskers, typically characterized by low curvature and thickness exceeding 1µm, with lengths extending into hundreds of µm. These whiskers feature a faceted lateral surface and a hexagonal cross-sectional shape. Their growth direction is aligned with {0001}. The catalyst drops situated on the whiskers frequently display an uneven, roughened surface with cracks and deformations (Novak et al. in 2020). In certain instances, whiskers can undergo the formation of radiating clusters composed of second-generation rods. Apart from rods and whiskers, Greenockite can also adopt a wire-like morphology, appearing as nanostructures with diameters less than 1µm and lengths extending to several hundreds of µm. Like whiskers, these wires elongate along the {0001} direction and can exhibit faceted top surfaces with hexagonal cross-sections. These wires tend to be flexible, often curving and interlacing with one another. The diameter of the catalyst droplets atop the wire structures frequently surpasses their thickness by a significant margin. On occasion, wires may change their growth direction from {0001} to {01-10}, resulting in a transition in morphology from wires to rods. This phenomenon is associated with variations in growth conditions, particularly temperature (Novak et al. in 2020).

GREENOCKITE IN DIFFERENT TYPE OF DEPOSITS

Greenockite holds significant importance in mineralogy and geology due to its diverse occurrences in various types of mineral deposits. Its presence and characteristics can provide describes the geological processes, fluid interactions, and mineralization mechanisms in different deposit types. Table 1 shows the occurrence of Greenockite in different type of deposits. Significance of different occurrences of greenockite across distinct deposit types, can be understood by understanding the different deposits as given below.

a. **Stratiform Deposit:** Stratiform deposits of greenockite are typically found in the Lady Loretta deposit, located in northwest Queensland, Australia. This deposit represents a Proterozoic stratiform lead-zinc-silver deposit characterized by the occurrence of zincian greenockite. It formed during the Proterozoic geological era and is hosted within laminated sulfide mineralization layers. In this geological context, greenockite is intergrown with galena, sphalerite, and minor pyrite (Patterson, 1985). The presence of greenockite within a cadmium-enriched zone is most likely a result of its original deposition rather than subsequent metamorphism or recrystallization processes. While some evidence of recrystallization of sulfides has been observed in the deposit, including features like polyhedral "foam" textures in sphalerite, planar annealing-type twins in sphalerite, and microscale veining of sphalerite laminae by galena, this mild metamorphism is insufficient to explain the extensive cadmium-anomalous zone. Therefore, it is reasonable to conclude that greenockite's presence in this cadmium-enriched zone originated as an integral aspect of the initial mineralization process, indicative of unique geochemical conditions during its formation (Patterson, 1985).

b. **Metamorphosed:** These types of deposits are notably present in the Sterling Hill deposit, which is situated within the Reading Prong geological belt in Sterling Hill, New Jersey (Johnson et al., 1990). The geological belt stretches from Pennsylvania to Connecticut and encompasses a variety of metamorphic and igneous rocks originating from the Proterozoic Grenville era. The rock formations within this belt include the Losee metamorphic suite, gneisses, amphibolites, and plutonic intrusions, all of which were formed during the Grenville metamorphism. While the exact tectonic setting of their formation has suggested a range from a continental margin to a back-arc spreading basin or rift basin near the North American craton (Johnson et al., 1990).These rocks have undergone significant heat and pressure during the metamorphic process, leading to mineralization events. Dating indicates that these rocks have ages ranging from 1,000 to 1,790 million years ago, with evidence suggesting gradual cooling after the Grenville event. The Sterling Hill deposit, which is associated with greenockite, is situated within the Franklin Marble, and consists of various mineral layers. These layers likely formed during folding and brecciation processes associated with Grenville metamorphism. Within the deposit, sulfide minerals like sphalerite and galena, along with greenockite, are commonly found in proximity to faults, fractures, and reaction zones. While erosion has affected the deposit's size, it has remained a significant source of ore production, along with the nearby Franklin Furnace deposit (Johnson et al., 1990).

c. **Granites:** Greenockite-bearing rocks have been identified within the Kaffo Valley albite-riebeckite-granite, signifying a late-stage mineralization event after the formation of the granite itself. This discovery holds particular significance as it provides information about the distinct geological processes governing the genesis of greenockite (Butler and Thomson, 1967b). The study underscores the role of post-consolidation albitization, a transformative geological phenomenon that has significantly altered the composition of the ultra-late-stage Kaffo Valley albite-riebeckite-granite. This alteration has had a profound impact on mineral associations and has induced fluctuations in Zn/Cd ratios.Expanding the scope of analysis to include the Odegi Complex, the study reveals variations in the concentrations of Cd and Zn among different rock types. Notably, the most recently formed rocks exhibit the highest Zn concentrations, while the earliest-formed rocks contain the greatest Cd concentrations. These variations emphasize the intricate and multifaceted nature of mineralization processes within these geological formations. However, it is worth noting that specific details regarding the tectonic setting remain undisclosed in the study (Butler and Thomson, 1967b).

d. **Sediment-hosted Pb-Zn deposit:** The formation of greenockite within the lead-zinc (Pb-Zn) deposits of the Zawar region is intricately linked to the complex geological history of this area. Located in the Udaipur district of Rajasthan, India, the Zawar region is renowned for its geological heritage, characterized by significant lead-zinc deposits (Jain and Bansal, 2003). These deposits are associated with the Aravalli Supergroup, a geological unit dating back to the Proterozoic era. Although the precise age of greenockite formation in this region is not explicitly mentioned in the available literature, it is generally attributed to the Proterozoic era, aligning with the broader geological context of the Aravalli Supergroup.In terms of mineralogy, greenockite is identified as a secondary mineral, formed through intricate geological processes. Within the Zawar region, greenockite is commonly found alongside sphalerite (ZnS), highlighting the close relationship between cadmium and zinc during the mineralization process. It is plausible that the formation of greenockite occurred as a result of hydrothermal mineralization processes. The influx of hydrothermal fluids, enriched with cadmium, likely led to interactions with pre-existing sphalerite, ultimately resulting in the precipitation of greenockite (Jain and Bansal, 2003; Sinha and Choudhary, 2006; Kumar and Tewari, 2015). The specific geochemical conditions prevailing during mineralization, including factors such as temperature, pressure, pH, and the presence of cadmium, played a crucial role in the genesis of greenockite. Importantly, the mineralization in the Zawar region may exhibit variations in cadmium and zinc geochemistry. The formation of greenockite may not be limited to the initial stages of ore deposition; it could also occur during subsequent phases or post-deposition alteration processes. Such occurrences could be triggered by changes in the local geological environment, including alterations in fluid composition and temperature. These changes may lead to the transformation of pre-existing sphalerite into greenockite. The presence of greenockite within the Pb-Zn deposits of the Zawar region provides valuable insights into the geological evolution of this area. It underscores the intricate interplay of hydrothermal activity, nuanced geochemical conditions, and potential post-deposition alterations, all contributing to the fascinating geological history of the region (Jain and Bansal, 2003; Sinha and Choudhary, 2006; Kumar and Tewari, 2015).

e. **Felsic Associations:** In the Kudriavy volcano, greenockite mineral was associated with the fumaroles. Situated on Iturup Island within the Kuril Islands chain in the Pacific Ring of Fire, this location is renowned for its tectonic activity. While specific details regarding the age and geological setting are not provided, the research sheds light on crucial aspects of mineralization in this dynamic region (Chaplygin et al., 2007). Greenockite, in association with felsic rocks, has been identified on Iturup Island within the Kuril Islands chain in the Pacific Ring of Fire. Samples collected and analyzed reveal the presence of solid solutions within the ZnS–CdS system, with a particular focus on Zn–Cd sulfides located in the fumaroles of the Kudriavy volcano (Chaplygin et al., 2007). The fumarolic environment surrounding the Kudriavy volcano, characterized by the dynamic flow of gases, suggests the significant role of gas-transport reactions in the genesis of these minerals. The mineralogical data, complemented by temperature measurements, provides compelling evidence of a miscibility gap within the natural ZnS–CdS system at high-temperature hydrothermal mineralization ranges. This comprehensive exploration unravels the complex geochemical dynamics within this geologically captivating and dynamic setting (Chaplygin et al., 2007).

f. **Gabbroic Association:** Greenockite is a mineral of particular interest, especially in its formation at the Baula site. It is unlikely that greenockite formed as a primary phase crystallizing from a gabbroic magma, as several Platinum Group Elements (PGE) deposits, including Baula, are believed to have originated through the fluid-assisted remobilization of PGEs. In the case of Baula, PGE mineralization appears to have occurred in two stages: magmatic and magmatic-hydrothermal. The latter stage involved post-liquidus deuteric alteration and hydrothermal remobilization. While it's important to note that there is no concrete evidence suggesting that the latter stage is a product of the remobilization of earlier sulfide deposits, it is thought that Pd-Te-Bi phases formed due to local remobilization, redistribution, and recrystallization of magmatic PGE-bearing Base Metal Sulfide (BMS) phases during late-stage hydrothermal alteration(Mishra and Hazarika, 2015). The geological matrix found in Baula, consisting of a chalcopyrite-pyrrhotite-pentlandite assemblage, is consistent with many mafic-ultramafic hosted magmatic sulfide-PGE deposits. What sets Baula's greenockite apart is the enigmatic absence of sphalerite or shadlunite, which are typically primary sources of Cd. Greenockite at Baula is mostly associated with siderite micro-veins in contact with chlorite. This suggests the occurrence of another fluid-induced alteration event, albeit not pervasive, during or after the last chlorite stage. The dissolved CO_2 content of the related fluid likely played a role, with Fe being supplied from chlorite and/or Fe (±Ni) sulfides. Remobilization of magmatic PGEs has been associated with CO_2-bearing, neutral to alkaline, and reduced fluids, favoring the transport of PGEs as bisulfide complexes. LA-ICP-MS data of chalcopyrite at Baula indicates an increase in the content of most trace elements closer to siderite micro-veins, except for Cd, which shows a notable decrease. This may suggest trace element enrichment by a later fluid that precipitated siderite and greenockite, possibly with contributions from silicates (Ti, Sr, Y, Zr, Ba from chlorite) and sulfides (Co, Ni from pentlandite) that equilibrated with the later fluid (Mishra and Hazarika, 2015). The reduction in Cd content could be explained by fluid-assisted leaching of Cd from chalcopyrite by a CO_2-bearing, low-temperature, neutral to alkaline, and reduced fluid that transported Cd as a bisulfide complex. The exclusive occurrence of greenockite and siderite together at Baula suggests their synchronous precipitation, possibly driven by a chemical reaction involving H_2O-CO_2 fluid, Fe, and Cd (Mishra and Hazarika, 2015).

Table 1: Deposits of Greenockite

Location	Rock or Ore Type	Host Rock	Reference
Joplin, Missouri	Mississippi Valley-type deposit	Jasperoidandcalcite-chert breccia	Cornwall, 1902
Asunta Sn-Ag deposit, Bolivia	Mineralized breccia in Ordovician metamorphosed shale	Hydrothermal veins	Ahlfeld, 1940
Tsumeb, South Africa	Aplite	Carbonate, chert, and shale	Hurlbut, 1957
Los Blancos, Spain	Sphalerite-galena ores of chloritized late-Tertiary volcanics and alteration zones	Schist, quartzite and phyllite	Oen et al., 1974
Sterling Hill, New Jersey	Cambrian-Ordovician gneiss and marble	Marble	Dunn, 1979
Lady Loretta, Queensland	Proterozoic stratiform sedimentary Pb-Zn-Ag deposit	Shale and siltstone	Patterson, 1985
Madjarovo ore district, Bulgaria	Proterozoic metamorphic and Mesozoic to Paleogene volcanics and sub-volcanics	Quartz-sulfide vein	Tarkian and Bresova, 1989

Sterling Hill, New Jersey	Metamorphic	metamorphic suite, gneisses, amphibolite	Johnson et al., 1990
Pb-Zn deposit, Zawar, India	Massive sulphide deposit	Dolomite	Holler and Gandhi, 1997
Local Boy ore zone, Babbitt deposit, Duluth Complex, Northeastern Minnesota	Gabbroic Rock	Association with Sphalerite	Hauck and Severson, 2000b
Tinos Island, Hellas	Epithermal polymetallic Ag–Au–Te mineralization	Coexists with wurtzite, siderite, smithsonite and magnetite.	Tombros et al., 2005; 2007; 2008
Kudriavy volcano, Iturup island, Kuriles, Russia	Fumaroles of Kudriavy volcano	Sphalerite	Champlygin et al., 2007
Caledonia group mines, blanca creek, la huerta range, San juan province, Argentina	Several ore minerals in varying parageneses	Sulfide mineralization	Mogessie et al., 2009
La Platina deposit, Chile	Low sulphidation epithermal deposits with polymetallic mineralization.	Cu-Ag deposit	Varas et al., 2015
Bangur Gabbro, Baula-Nuasahi Complex, Eastern India	chromite-PGE-base metal sulfide association	siderite micro-veins	Mishra and Hazarika, 2015
Saishitang Cu Skarn Deposit, Qinghai Province, Northwest China	Hydrothermal	intrusions, metamorphosed tuff, and marble-containing metamorphosed siltstone	Liu and Zhang, 2017
Upper Silesia, Poland	fumarole	aggregates	Nowak et al., 2020
Bagada orogenic gold prospect, Paleoproterozoic Mahakoshal belt, Central Indian Tectonic Zone (CITZ).	Hydrothermal deposit	Metasediments and metavolcanic rocks with intrusions of syenites, ultramafic rocks, variety of alkaline rocks	Baswani et al., 2023

CONCLUSION

Cadmium, a versatile transition metal in earth's crust in form of greenockite, holds significant scientific and societal importance. This comprehensive review explores into greenockite's multifaceted significance, shedding light on its distribution, geochemistry, and diverse occurrences. By filling knowledge gaps and building upon foundational research, this paper offers valuable insights into its geological importance, emphasizing its role in resource prospecting, technological innovation, and responsible material management. It forms in specific geological conditions, often within hydrothermal ore deposits. It typically arises as a secondary mineral after primary mineral crystallization in cadmium-rich fluids. Its formation involves the interplay of cadmium and sulfur ions in these hydrothermal solutions, with temperature playing a crucial role. This mineral's geological presence spans diverse settings, such as metamorphosed zinc oxide mineralization, granites, fumaroles, pegmatites, and sediment-hosted Pb-Zn deposits, with notable exceptions like the Babbitt deposit in gabbroic rock. Experimental research has illuminated the factors influencing greenockite formation, including solid solubility, precipitation mechanisms, pH levels, and fluid composition. It often replaces zinc minerals, primarily sphalerite, depending on the abundance of cadmium and zinc in hydrothermal fluids. The relatively low formation temperature of 100°C to 200°C underscores its thermodynamic stability. Its association with hydrothermal ore deposits occurs in diverse geological settings, from sedimentary and metamorphic rocks to regions with volcanic activity. It exhibits a hexagonal crystalline structure known as the zinc blende structure. Its crystals come in various morphological forms, including rods, wires, and whiskers, often with bismuth drops on crystal tops. These forms exhibit distinct facets and growth directions, further adding to the mineral's complexity and scientific intrigue. Its vibrant coloration, ranging from pale yellow to deep orange-red, is linked to cadmium concentration within its lattice. Greenockite's optical properties, including anisotropic behavior, make it valuable for optoelectronic applications. Researchers have reported solid solubility within the ZnS-CdS system at high temperatures but also observed immiscibility under certain conditions. The temperature at which it forms and its replacement of Cd by Zn are influenced by these factors, as well as oxygen fugacity, hydrogen sulfide activity, and chloride ion content in the fluid. Its presence in various deposit types sheds light on its relation with diverse geological processes. In the Lady Loretta deposit, Queensland, Australia, greenockite occurs in Proterozoic stratiform lead-zinc-silver deposits, intergrown with galena and sphalerite. Found in Sterling Hill, New Jersey, within Proterozoic Grenville-era metamorphic rocks. Sulfides like sphalerite and galena, along with greenockite, occur near faults and fractures. Greenockite is associated with late-stage mineralization in the Kaffo Valley albite-riebeckite-granite, indicating post-consolidation albitization processes. In the Zawar region, India, greenockite forms due to hydrothermal mineralization processes, often alongside sphalerite. In the Kudriavy volcano fumaroles, Iturup Island, solid solutions of ZnS–CdS have been observed, suggesting gas-transport reactions in mineral genesis.At the Baula site, greenockite is associated with PGE mineralization, possibly due to remobilization of PGE-bearing minerals during hydrothermal alteration. Its presence alongside siderite indicates later fluid-induced alteration events. It is primarily associated with specific geological settings but is also found as a secondary product in certain other geological processes, subject to ongoing research.

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