Bulletin of Pure and Applied Sciences
Geology (Geological Science), Vol.42F, No.2,
July-December 2023: P.211-218
Original Research Article

Print version ISSN 0970 4639
Online version ISSN 2320 3234
DOI: 10.48165/bpas.2023.42F.2.4
Available online at www.bpasjournals.com

Rhenium in the Earth's Crust: A Comprehensive Review of Mineralogy, Geochemistry and Economic Significance

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(Received on 17.06.2023, Revised on 13.08.2023, Approved on 17.09.2023, Accepted on 05.10.2023, Published on 15.12.2023)

How to cite this article: Deshmukh S.N. and Varade A.M. (2023). Rhenium in the Earth's Crust: A Comprehensive Review of Mineralogy, Geochemistry and Economic Significance.*Bulletin of Pure and Applied Sciences- Geology*,42F(2), 211-218.

Abstract:
Rhenium, a unique and valuable metal with exceptional properties which is vital in various industrial applications, primarily found in conjunction with minerals like molybdenite and chalcopyrite, predominantly in western countries. Despite its rarity, understanding its geological distribution, geochemical characteristics, atomic structure, and behavior is essential. This paper provides a concise overview of the geological and geographical occurrences of rhenium, shedding light on its formation within both igneous and sedimentary environments. Additionally, it examines its economic significance, emphasizing its critical role in industries like aerospace, electronics, and petrochemicals due to its high-temperature resistance, corrosion resistance, and electrical conductivity enhancement. This comprehensive exploration highlights the importance of rhenium as a byproduct of mining, contributing significantly to technological advancements and innovation across various sectors.

Keywords: *Rhenium, Geochemistry, Molybdenite, Chalcopyrite, Economic Implications*

INTRODUCTION

In the world of science and technology, there is a special metal known as 'Rhenium' (Re). It is element number 75 on the periodic table, and it has some unique qualities that make it incredibly valuable in many different areas. It can handle high heat, remains unaffected by rust, and is exceptionally strong. These characteristics have caught the attention of experts, making Re a crucial part of many applications. Whether it is ensuring toughness in aerospace or enhancing conductivity in electronics, Re's diverse contributions have left a lasting impact on scientific progress and innovation. Understanding Re's geological occurrence is essential as it lacks in earth's crust. Rhenium's abundance is estimated to be around 1 part per billion by weight, making it one of the rarest elements. As industries increasingly rely on Re for critical applications, comprehending its geological distribution becomes essential for sustainable resource management and strategic planning. Mining and extracting Re-bearing ores require knowledge of the specific geological formations where Re is found in conjunction with other valuable minerals, such as molybdenum (Frenzel et al., 2005). Mapping these geological settings aids in identifying potential sources of Re, which is often obtained as a byproduct during the processing of molybdenum ores. By understanding the geological contexts that give rise to rhenium deposits, industries can optimize their extraction processes, minimize environmental impact, and ensure a stable supply of this valuable resource.

This paper explores the detailed about the Re in the earth's crust and its many uses. Re has special qualities that make it important in science, industry, and technology (Hattendorf and Günther 2003). But to make the most of it, we need to understand where it comes from in the earth's crust. The primary purpose of this paper is to provide a review of Re's geological presence, mineralogical associations, its atomic structure, and the potential it holds as a strategic resource. The paper seeks to bridge the gap between Re's unique attributes and its geological context, thereby shedding light on its important occurrences within earth's crust. Through an interdisciplinary lens, this review aims to inform researchers, geologists, and industry professionals about rhenium's intricate distribution and the implications it carries for technological advancements, particularly in aerospace and electronics (Gupta 2007). This paper aims to enhance our comprehension of the distribution of Re by conducting a thorough examination of its geological occurrences and their associations with specific mineralogical environments. Furthermore, through an exploration of the economic considerations linked to Re, this paper seeks to substantiate the significance of this element. Ultimately, this synthesis of geological and industrial perspectives seeks to unravel the complexities of Re and amplify awareness about its potential significance in modern science and technology.

GEOLOGICAL AND GEOGRAPHICAL OCCURRENCES OF RHENIUM

Re's geological occurrence is closely linked to specific mineral deposits and geological processes. Re is often associated with various types of sulfide minerals, such as molybdenite (MoS_2) and porphyry copper deposits, where it substitutes for other transition metals in their crystal structures (Hagni et al., 2017). These deposits typically form in magmatic-hydrothermal systems, where high-temperature fluids interact with host rocks, leading to the concentration of various elements including rhenium (Sillitoe, 2010).Another notable geological occurrence of Re is in certain sedimentary environments. Organic-rich marine sediments, such as black shales, can contain elevated concentrations of rhenium due to its affinity for binding to organic matter during sedimentation (Peucker-Ehrenbrinkand Ravizza., 1995). As these sediments undergo diagenesis and become sedimentary rocks, Re can become enriched, resulting in its accumulation within the rock matrix (Ravizza and Turekian, 1989). Examples of rhenium-enriched black shale formations include the Green River Formation in the United States and the Kimmeridge Clay Formation in the United Kingdom (Peucker-Ehrenbrink et al., 1995). In both magmatic-hydrothermal and sedimentary settings, the geological processes involved in the formation of these deposits play a crucial role in determining the abundance and distribution of rhenium. Re's presence offers an understanding of Earth's internal processes.

Re substitutes for molybdenum in the crystal lattice of molybdenite, resulting in its enrichment within these deposits (Stein et al., 1998). This association is particularly relevant due to the economic significance of porphyry copper deposits, where molybdenum and rhenium are considered valuable byproducts (Kesler et al., 2005). Additionally, the discussion extends to the role of Re in platinum-group minerals (PGMs), such as pentlandite and chalcopyrite, which are often found in magmatic sulfide deposits. Re's affinity for these minerals is attributed to its similar chemical behavior to other platinum-group elements (PGEs) (Naldrett et al., 1999). The presence of Re in these minerals contributes to its broader distribution within the Earth's crust.

Re is a relatively rare element with a limited geological distribution, with approximately 80% of the world's rhenium found in the western countries. Notable occurrences include deposits in Chile, the United States, Peru, and Poland. In Chile, a major producer of Re, it is extracted as a byproduct of copper mining due to the presence of varying Re amounts in copper ores (Castillo et al., 2018). The United States contributes significantly to global Re production, mainly through molybdenum mining in regions like Colorado and Utah, where molybdenum ores, particularly molybdenite (MoS_2), contain trace rhenium (USGS, 2021). Peru, known for rich mineral resources, recovers Re from copper mining activities, akin to Chile. Poland, recognized for molybdenite deposits, diversifies global rhenium production through potential byproduct extraction in molybdenum mining operations. These countries are essential in the global supply chain of this strategic metal, extracted as a valuable byproduct from copper and molybdenum ores, underscoring Re geological importance.

In the context of India, the Singhbhum Copper Belt has a Re occurrences. The mineralization in this region has been dated to the Proterozoic era, around 1.8 to 2.5 billion years ago (Bhattacharjee et al., 2018). The formation of these deposits is attributed to the interaction of hydrothermal fluids with the host rocks, resulting in the mobilization and concentration of copper, molybdenum, and Re. The minerals associated with Re include chalcopyrite, bornite, and molybdenite. These deposits provide detailed insight implications for understanding metallogenesis.

GEOCHEMISTRY OF RHENIUM

Studying Re-enriched deposits, including their occurrence, age, formation processes, associated minerals, and geochemistry, offers details of geological distribution. Re’s presence in minerals like molybdenite is intricately tied to factors such as temperature, pressure, and sulfur levels during mineral formation (Hagni et al., 2017).In porphyry copper-molybdenum deposits, Re is associated with molybdenite, a sulfide mineral that forms during the late stages of magmatic-hydrothermal systems. These systems are created when magma intrudes into the earth's crust, causing hydrothermal fluids to circulate and interact with surrounding rocks. This process leads to the deposition of minerals like molybdenite, with Re substituting for molybdenum within their crystal structures.

Geochemical studies of these deposits involve analyzing trace element concentrations, isotopic compositions, and mineralogical associations to decipher the processes that led to rhenium enrichment. The geochemical behavior of Re is influenced by several factors, including its compatibility with minerals during crystallization, its solubility in hydrothermal fluids, and its affinity for sulfide minerals (Mungall and Brenan, 2014). The mobility of Re in hydrothermal fluids is affected by various chemical conditions such as temperature, pressure, pH, and sulfur fugacity. Re is known to preferentially partition into sulfide phases during magmatic processes, leading to its enrichment in sulfide-rich minerals like chalcopyrite ($CuFeS_2$) and molybdenite. These factors influence the speciation of rhenium in solution and its ability to form complexes with other elements. Understanding its geochemical behavior helps in identifying potential sources of rhenium and optimizing its extraction and utilization.

(a) Crystal Structure of Rhenium:

Re's presence in molybdenum minerals such as molybdenite (MoS_2) is of particular interest due to their chemical similarity and the tendency of Re to substitute for molybdenum in the crystal lattice. Molybdenite is a layered sulfide mineral consisting of sheets of molybdenum and sulfur atoms. Re can readily replace molybdenum in these sheets due to their similar atomic sizes and comparable chemical properties. In the crystal structure of molybdenite, each molybdenum atom is coordinated with six sulfur atoms in a trigonal prismatic arrangement. When Re substitutes for molybdenum, the crystal structure remains largely unchanged, as Re can fit into the same coordination environment due to its similar bonding characteristics (Takahashi et al., 2007). This substitution of Re into the molybdenum lattice is significant because it can affect the physical and chemical properties of molybdenite and has implications for the economic extraction of both elements.

For identification of exact structure, various analytical techniques, such as X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) were used by various scientist. The XANES spectra, which provide information about the chemical state of an element, were compared between Re in molybdenite and reference materials like ReS2 and Re metal. The crucial observation was that the XANES peak of Re in molybdenite closely resembled that of Re (IV) S2 and Re metal (Takahashi et al., 2007). This similarity hinted at a shared atomic environment between Re in molybdenite and these reference materials. Furthermore, the oxidation state of Re in molybdenite was investigated, and the results indicated that it exists primarily in the Re (IV) state. Importantly, the study demonstrated that Re(IV) could effectively replace Molybdenum (Mo) in molybdenite (Takahashi et al., 2007) EXAFS analysis revealed that the atomic structures of Re in molybdenite and ReS_2 were remarkably like that of Mo in molybdenite. This similarity supported the idea that Re could substitute for Mo within the crystal lattice of molybdenite. Detailed measurements of coordination numbers and interatomic distances were conducted for different atomic shells in both molybdenite and ReS_2. Notably, the Re-S distance in molybdenite closely matched the Mo-S distance in the same mineral. Therefore similarity between Re in molybdenite and ReS_2, highlighting the potential for Re (IV) to substitute for Mo(IV) in the mineral's structure (Takahashi et al., 2007).

Re's presence in chalcopyrite is notable for its potential impact on the behavior of both copper and Re during mineralization processes. In the crystal structure of chalcopyrite, copper and iron atoms are coordinated with sulfur atoms in a tetrahedral arrangement, forming a lattice of interconnected tetrahedra. Re can substitute for both copper and iron in the chalcopyrite lattice, although its preference for either site may depend on various geochemical conditions. The substitution of Re into chalcopyrite can influence the mineral's electronic properties, conductivity, and reactivity. Additionally, Re's incorporation into chalcopyrite has implications for the economic extraction of both elements from ore deposits, as Re-rich chalcopyrite can affect the overall value of the mineral resource. Re's incorporation into the crystal structures of minerals like molybdenite and chalcopyrite highlights its ability to substitute for other elements due to its similar atomic size and bonding characteristics. Understanding the crystallographic behavior of Re in these minerals is crucial for both scientific understanding and practical applications, such as mineral exploration and processing (Nebeker and Hiskey, 2012 and Takahashi et al., 2007).

(b) Geochemical behavior of Rhenium:

Various types of mineral deposits serve as hosts for Re, with key categories including granitic-related deposits (such as porphyry, skarn, and quartz-vein deposits), sediment-hosted stratabound/stratiform Cu deposits, uranium (U) deposits, and magmatic sulfide deposits, among others. Porphyry Cu-Au-Mo deposits are globally significant sources of both Mo and Re. Interestingly, molybdenite from these deposits, including porphyry Cu and Cu-Au deposits, tends to contain significantly more Re than that found in Mo-dominated porphyry Mo systems. These porphyry deposits collectively account for a substantial portion (approximately 85% to 90%) of the world's primary Re production, primarily as a by-product of molybdenite. The Re grades in these deposits typically range from 0.1 to 0.5 ppm (Zhao et al., 2023). Other granite-related deposit types, like skarn deposits and quartz-vein deposits, also host Re, and it is believed that molybdenite predominantly carries Re in these deposits. Cu and Cu-Au skarns generally contain molybdenite with lower Re concentrations than Fe and Au skarn systems, similar to porphyry deposits where Mo skarns have lower average Re concentrations compared to Cu-Mo skarns. Sediment-hosted Cu deposits, often stratabound or stratiform, differ in their Re hosting. These deposits primarily contain Cu- and Cu-Fe sulfides disseminated throughout the mineralization. Unlike granite-related deposits, Re in sediment-hosted Cu deposits is primarily hosted by Cu minerals rather than molybdenite. The Re grades in sediment-hosted Cu deposits, such as Lubin and Dzhezkazgan, are higher, around 1 ppm (Zhao et al., 2023). Sandstone-hosted U deposits, while accounting for a smaller portion of world Re production (approximately 1%), are known to be enriched in Re. Re is thought to be closely associated with Mo and may be concentrated in jordisite, an amorphous Mo mineral, with some Re found in U minerals like uraninite and in organic matter (Zhao et al., 2023). Magmatic sulfide deposits, formed through the separation of sulfide liquids from mafic or ultramafic silicate magmas, represent another potential source of Re. While the Re grades for these deposits are not yet available, they are unique in that they produce almost no Mo. It is suggested that sulfides responsible for concentrating platinum group elements (PGEs) could also play a role in concentrating Re in these deposits due to Re's highly siderophile and chalcophile nature. Various studies indicate that sulfides, particularly molybdenite, are common hosts for Re in Re-bearing deposits. Additionally, some Re may also be concentrated in U minerals and organic matter within these systems. Understanding the diverse hosting mechanisms is essential for comprehending Re's geochemical behavior in different geological contexts (Zhao et al., 2023).

Re exhibits a robust affinity for sulfur compounds and the possibility of co-precipitating with iron sulfides. Notably, there are clear disparities in how Re behaves when compared to Mo and W. This emphasizes the critical significance of accounting for the unique chemical speciation of trace elements when investigating their geochemical behaviors in various geological environments. These discoveries enhance our comprehension of Re's role within natural systems and its importance in geochemical processes (Akintomide et al., 2021).

Hydrothermal systems play a pivotal role in the mineralization of Re, contributing to its enrichment within various geological settings. These systems are characterized by the circulation of hot aqueous fluids within the Earth's crust, driven by heat generated from magma or other subsurface processes (Sillitoe, 2003). Re becomes mobilized within these fluids, often in the form of soluble Re species, as they interact with host rocks and minerals. As the hydrothermal fluids traverse through fractures and pore spaces, they carry dissolved Re and other elements, eventually precipitating them as mineral deposits when the conditions for deposition are met. One prominent example of Re mineralization in hydrothermal systems is found in porphyry copper-molybdenum deposits. These deposits form when magmatic intrusions bring heat and fluids into the surrounding rocks. As these fluids cool, they deposit minerals like molybdenite, a sulfide mineral containing Re. Re incorporation into molybdenite crystals occurs due to its affinity for sulfides and its substitution for molybdenum in the crystal lattice. Over time, the hydrothermal fluids facilitate the accumulation of Re-enriched minerals, creating valuable resources for industrial applications (Hagni et al., 2017 and Sillitoe, 2010). The formation of hydrothermal systems and subsequent mineralization of Re are dynamic processes influenced by a range of factors such as temperature, pressure, fluid composition, and geological environment. Understanding the interplay between these factors allows researchers to predict the occurrence of Re-rich deposits in specific settings, contributing to the sustainable utilization of this valuable metal.

Sedimentary environments also host Re, particularly in organic-rich black shales. These shales accumulate in marine basins over long periods and contain organic matter that sequesters rhenium during sedimentation. As organic material decays and undergoes diagenesis, rhenium is released and can become concentrated in the shales (Zhao et al., 2023).

Geochemical behavior of Re was thoroughly understood by focusing on its role in different geological contexts such as arc magmas and Mid-Ocean Ridge Basalts (MORB) (Li, 2014). In the early stages of differentiation within oxidized arc magmas, elements like Ytterbium (Yb), Copper (Cu), Gold (Au), Silver (Ag), and Re exhibit similar distribution patterns, with bulk partition coefficients (D) that are approximately equal. However, as differentiation progresses, these coefficients change significantly. Cu, Au, and Ag are primarily influenced by crystalline monosulfide solid solution (MSS), while Re behavior is mainly controlled by magnetite. Notably, Re demonstrates a lower partition coefficient in the MSS/silicate melt system compared to the other elements (Li, 2014). In contrast, MORB rocks are typically saturated with sulfide liquid, and a positive correlation has been observed between Cu and Re partition coefficients and oxygen fugacity, irrespective of sulfur content. This suggests that Re behavior during MORB differentiation is sensitive to changes in oxygen fugacity, with implications for its compatibility under different redox conditions. Additionally, Ytterbium (Yb) behaves as an incompatible element during MORB differentiation, leading to an increasing Yb/Re ratio with decreasing magnesium oxide (MgO) content. While the role of sulfide liquid in controlling Re geochemical behavior during MORB differentiation remains a subject of ongoing research, these findings deepen our understanding of the complex interplay of elements in geological processes, offering valuable insights into Earth's crust and mantle dynamics (Li, 2014).

In the Wuliping deposit, the remarkable discovery of elevated Re concentrations averaging approximately 28 ppm challenges conventional Re-bearing deposit norms, where Re content typically ranges from 0.1 to 0.5 ppm. Notably, this high Re content is uniquely hosted by Re-rich clay minerals, distinct from established Re-bearing deposit types such as granite-related, sediment-hosted Cu, U, and magmatic sulfide deposits, where molybdenite or sulfides are the primary hosts. The Wuliping deposit appears to represent a novel ion-adsorption Re deposit, akin to ion-adsorption rare earth element (REE) deposits. This distinctive Re enrichment likely originated from weathering processes, driven by the decomposition of primary molybdenite-bearing rocks in the Shangsi Formation. The study highlights the potential for clay minerals to play a key role in forming economic Re mineralization in ion-adsorption deposits, though further investigation is needed to fully understand the transition process from primary Re-bearing minerals to Re-rich clay minerals (Zhao et al., 2023). In case of Chengmenshan deposit of a typical porphyry-skarn deposit in the Middle-Lower Yangtze River Valley Metallogenic Belt, Re primarily associated with molybdenite in a diverse array of critical metals. The distribution of these metals exhibits a spatial pattern that shifts from molybdenum and Reto copper, cobalt, selenium, tellurium, and gallium Furthermore, the enrichment of cobalt, cadmium, and indium within the deposit is closely tied to changes in fluid temperature, emphasizing the dynamic geological processes at play in this complex ore system of Re (Gua et al., 2023).

During the extraction and processing of molybdenum ores, Re becomes co-extracted due to its substitution for molybdenum within the molybdenite crystal lattice. This phenomenon is particularly significant in porphyry copper-molybdenum deposits, which are characterized by the presence of molybdenite-bearing ores. These deposits result from magmatic-hydrothermal processes, where magma intrusion and subsequent fluid circulation create mineralized zones. Re chemical similarities to molybdenum enable it to substitute readily into the molybdenite structure. As a result, Re becomes incorporated into the molybdenum concentrates obtained from these deposits.

ECONOMIC SIGNIFICANCE

Rhenium, a valuable and relatively scarce transition metal, often emerges as a byproduct of molybdenum mining operations. Molybdenum, a critical element in various industrial applications, is commonly found in mineral deposits containing molybdenite (MoS_2) (Werner et al., 2023). The assessment of global and regional rhenium reserves is crucial in understanding the potential supply of this valuable metal and its economic significance. Rhenium is relatively rare in the Earth's crust. Estimating Re reserves involves evaluating the known deposits, their associated minerals, and the prevailing geological conditions. Re scarcity makes it challenging to quantify its global reserves accurately. Prominent regions with significant rhenium production include Chile, the United States, and Kazakhstan. However, due to its association with specific minerals and the dynamic nature of mining operations, global Re reserves are subject to fluctuations based on market demand and economic feasibility. Assessing regional rhenium reserves requires a detailed analysis of specific mineral deposits and their Re content. Rhenium's exceptional properties make it indispensable in various industries. Aerospace relies on Re-containing superalloys for engine components, while electronics use it in electrical contacts and X-ray equipment. The petrochemical sector benefits from rhenium-based catalysts, and the emerging renewable energy sector also seeks rhenium for its potential applications. One of the most notable applications of Re lies in aerospace industries. Its remarkable resistance to high temperatures, combined with its excellent mechanical properties, makes it an essential component in the manufacturing of aircraft engines and gas turbine components. Rhenium-containing super alloys exhibit exceptional performance under extreme conditions, allowing engines to operate efficiently at elevated temperatures and pressures, enhancing both fuel efficiency and performance. In the electronics sector, Re is employed in the production of electrical contacts and filaments. Its high electrical conductivity and stability at elevated temperatures contribute to the reliability and longevity of electronic devices. Moreover, Re is a critical component in the production of X-ray tubes and detectors due to its ability to emit X-rays upon bombardment with electrons. Re presence in superalloys and catalysts used in the petrochemical industry further highlights its importance. The addition of rhenium enhances the strength, corrosion resistance, and longevity of superalloys used in jet engine components and industrial machinery. Re-based catalysts play a vital role in catalytic reforming processes, enabling the production of high-octane gasoline and various petrochemical products (Kesieme et al., 2019).Restatus as a byproduct of mining, coupled with its exceptional properties, holds immense implications for various industrial sectors. Its contributions to aerospace, electronics, petrochemicals, and other fields underscore its indispensable role in advancing technology and innovation.

CONCLUSION

Rhenium is a unique and valuable metal with extraordinary properties. Approximately 80% of the world's rhenium is found in specific countries, including Chile, the United States, Peru, and Poland, primarily as a byproduct of copper and molybdenum mining operations. It is often associated with specific mineral deposits and geological processes, primarily found in sulfide minerals like molybdenite and porphyry copper deposits. It is also enriched in sedimentary environments, particularly in organic-rich black shales. Geochemistry of Re is a complex interplay of factors. Its affinity for sulfur compounds is evident in various contexts, such as porphyry copper-molybdenum deposits, where it substitutes for molybdenum in minerals like molybdenite. Temperature, pressure, and sulfur fugacity influence Re's behavior in these environments, shedding light on crustal dynamics. Moreover, Re's presence in sedimentary formations underscores its intricate geochemical behavior during diagenesis and sedimentation. This knowledge is crucial for both scientific study and for industries that depend on this precious but uncommon metal. The economic significance of rhenium is highlighted by its vital role in aerospace, electronics, petrochemicals, and catalytic applications. Despite its scarcity, Rhenium's exceptional properties continue to drive innovation and technological advancements across various industries.

Conflict of interest:
Authors declares no conflict of interest

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