

Review

Research Status and Challenges of High-Purity Quartz Processing Technology from a Mineralogical Perspective in China

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Abstract: Quartz deposits are widely dispersed in nature, but the presence of ore bodies capable of yielding high-purity quartz is exceedingly rare. As a result, the effective purification and processing of high-purity quartz from natural siliceous materials has emerged as a prominent area of research within the non-metallic mineral processing field. This article offers an overview of the current state of research and its limitations in quartz purification and processing technology in China, including the characteristics of quartz mineral resources, the geological origins of ore deposits, impurity forms in ores, and purification techniques. Drawing from examples of five distinct types of quartz ores—vein quartz, powder quartz, quartzite, granitic pegmatite, and pegmatitic granite—we delve into the inherent properties of quartz deposits, ores, and minerals from a mineralogical perspective, establishing their link to purification and processing methodologies. A fundamental challenge restraining the advancement of the high-purity quartz industry is the absence of criteria for evaluating and selecting high-purity quartz raw materials. Existing purification technologies grapple with issues such as intricate single mineral liberation, substantial acid consumption, high energy requirements, and protracted processing procedures. The lack of mineralogically based deep purification techniques presents a hurdle to the development of the high-purity quartz industry. Given the diversity of ore types, the pursuit of knowledge-driven design and the development of economically efficient, environmentally friendly, and streamlined new technologies for tackling the complexities of the purification process may constitute the future direction of our endeavors.



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1. Introduction

High-purity quartz is a mineral obtained from natural siliceous materials after a series of physical and chemical purification processes. It exhibits specific particle size specifications and typically boasts an SiO₂ content exceeding 99.9%. Due to its remarkable physical and chemical properties, including high-temperature resistance, low thermal expansion coefficient, exceptional transparency, effective electrical insulation, and resistance to corrosion, it has wide-ranging applications in high-tech sectors such as electronics, intelligent manufacturing equipment, advanced inorganic non-metal materials, high-performance fibers and products, solar energy, and more [1]. As early as 2018, China's National Bureau of Statistics recognized the strategic importance of high-purity quartz mineral products in its 'Classification of Strategic Emerging Industries' [2].

Currently, countries worldwide have recognized high-purity quartz as a strategically significant resource. High-purity quartz products are categorized into four grades based on SiO₂ purity: ultra-high purity ($\omega(\text{SiO}_2) \geq 99.998\%$ or 4N8), high-purity ($\omega(\text{SiO}_2) \geq 99.995\%$ or 4N5), medium-purity ($\omega(\text{SiO}_2) \geq 99.99\%$ or 4N), and standard-purity ($\omega(\text{SiO}_2) \geq 99.9\%$ or 3N). Abroad, extensive production of 4N grade high-purity quartz is already established, with these deposits primarily located in regions including North Carolina in the United States, Nordland County in Norway, Khanty-Mansi Autonomous Okrug in Russia, Queensland in Australia, and the Nuadibú Bay Province in Mauritania. Moreover, the purification and processing technology for 5N grade high-purity quartz has also reached a high level of maturity. For example, Unimin Corp in the United States can achieve impurity levels as low as 8 $\mu\text{g/g}$ in their products [3].

China indeed possesses abundant reserves of quartz mineral resources; however, the presence of ore bodies capable of producing high-purity quartz is exceedingly rare. Domestically, the production of high-purity quartz from natural crystal sources, exemplified by Jiangsu Pacific Quartz Co., Ltd., has been limited, with an annual capacity not surpassing 20,000 tons. Furthermore, much of this output is directed towards the preparation of medium-purity or standard-purity quartz products. As the resources of natural crystal-grade quartz gradually deplete, a looming shortage of high-quality quartz raw materials becomes evident. Concurrently, the outdated state of high-purity quartz preparation technology further exacerbates the severe mismatch between supply and demand. In 2020, China imported a staggering 144,500 tons of high-purity quartz, representing over 70% of the global import total. In 2022, the price of high-purity polycrystalline silicon surged from RMB 110,000 per ton in 2021 to RMB 270,000 per ton [4]. Consequently, the effective purification of quartz from natural siliceous materials has emerged as a central focus of current research.

Quartz, one of the Earth's most abundant minerals, is widespread in igneous, metamorphic, and sedimentary rocks. Under diverse geological conditions, it gives rise to various types of ore deposits, including natural crystal, quartz sandstone, quartzite, vein quartz, powder quartz, quartz sand, and granitic quartz. Quartz ores typically contain a multitude of impurity elements, associated/coexisting minerals, fluid inclusions, mineral inclusions, lattice impurities and hydroxyl impurities. These complexities make the purification process intricate, involving various complex steps such as pre-treatment, physical separation, chemical treatment, and advanced processing [5].

Pan et al. reviewed the distribution of high-purity quartz resources and their applications, summarized the various types of quartz ores and the characteristics of impurities, and elucidated the mechanisms behind different purification techniques [6]. Lin et al. provided an overview of quality assessment techniques and separation methods for high-grade quartz, with a focus on summarizing the thermal phase transitions of mineral inclusions, fluid inclusions, and trace elements within lattice structures [7]. Lin et al. also reviewed the current status, progress, and mechanisms of hydrometallurgy in the quartz purification process, including bioleaching, high-temperature leaching and high-pressure leaching [8]. It is worth noting that the formation of high-grade natural quartz deposits is constrained to specific geological environments. Consequently, from a mineralogical perspective, the purification potential of quartz is intrinsically linked to its ore deposit origin, ore characteristics, and mineral properties. However, most published research is focused on purification techniques and principles, with relatively limited attention to the mineralogical characteristics of quartz raw materials.

The purpose of this paper is to present an overview of China's quartz mineral resources, encompassing their reserves, the geological attributes of various quartz deposits, and the forms of impurities within the ores. Drawing upon five different types of ore examples from Jiangxi Province in China, including vein quartz, powder quartz, quartzite, granitic pegmatite, and pegmatitic granite, this study analyzes the impact of the mineralogical characteristics of the raw materials on the purification process, and then explores the inherent relationship between quartz deposits, ores, mineral prop-

erties, and its separability, thereby providing a theoretical guidance for the geological exploration and evaluation of high-purity quartz resources, as well as the selection of purification processes.

2. The Characteristics of Quartz Mineral Resources

2.1. The Reserves of Quartz Mineral Resources in China

As of 2022, the confirmed reserves of quartz mineral resources in China are depicted in Figure 1, with data sourced from the Ministry of Natural Resources of the People's Republic of China. From Figure 1, it can be observed that China possesses abundant siliceous mineral resources, with total reserves of quartzite and vein quartz reaching 1364.18 million tons and 82.1 million tons, respectively. In contrast, the reserves of powder quartz and crystal resources are relatively limited, standing at only 5.64 million tons and 4.19 million tons, respectively.

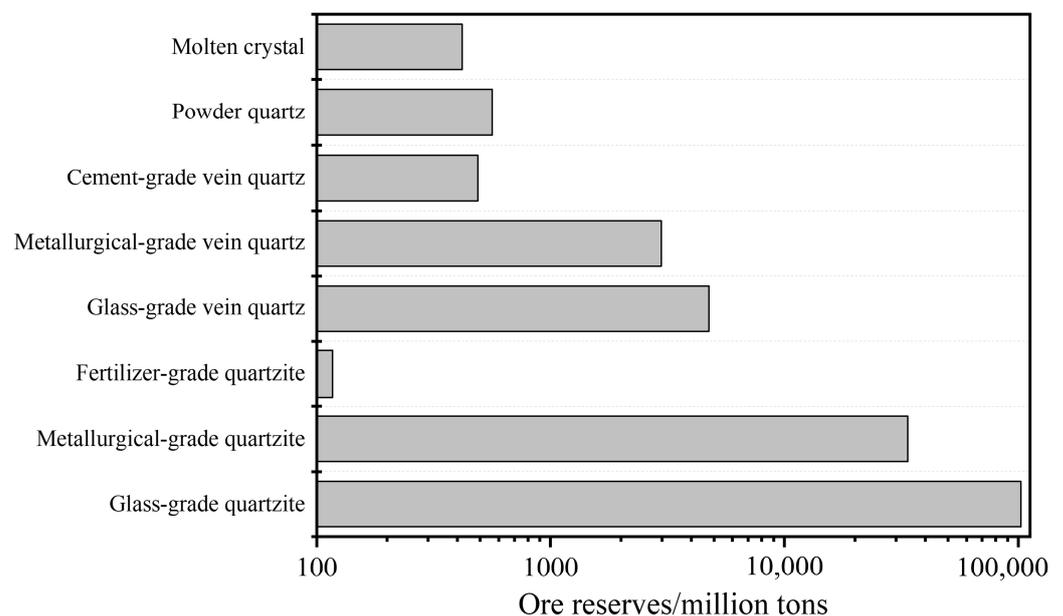


Figure 1. Statistics of confirmed quartz mineral resource reserves in China (as of 2022).

Taking Jiangxi Province in China as an example, the main mineral categories that have been explicitly categorized include natural crystal, powder quartz, quartzite, sandstone, quartz sand, and vein quartz. As of 2020, the mineral resource reserves in Jiangxi Province are depicted in Figure 2, with data sourced from the Digital Remote Sensing Center of the Jiangxi Geological Survey Institute.

From Figure 2, it can be observed that in terms of resource reserves, sandstone, quartzite, and quartz sand have the highest reserves, collectively accounting for approximately 90% of the total resource reserves. Vein quartz and powder quartz have relatively lower proportions, standing at only 5.79% and 4.23%, respectively. The confirmed resource quantity of natural crystal is extremely scarce, accounting for 1.7×10^{-7} of the totals. In terms of the number of deposits, vein quartz holds the highest proportion, followed by quartzite and sandstone, accounting for 22% and 15%, respectively. Powder quartz and quartz sand exhibit smaller shares, while natural crystal has the least number of deposits, approximately 1%. These results indicate that the reserves of natural crystal are exceedingly low, with most of them lacking scale, resulting in a relatively limited exploration prospect.

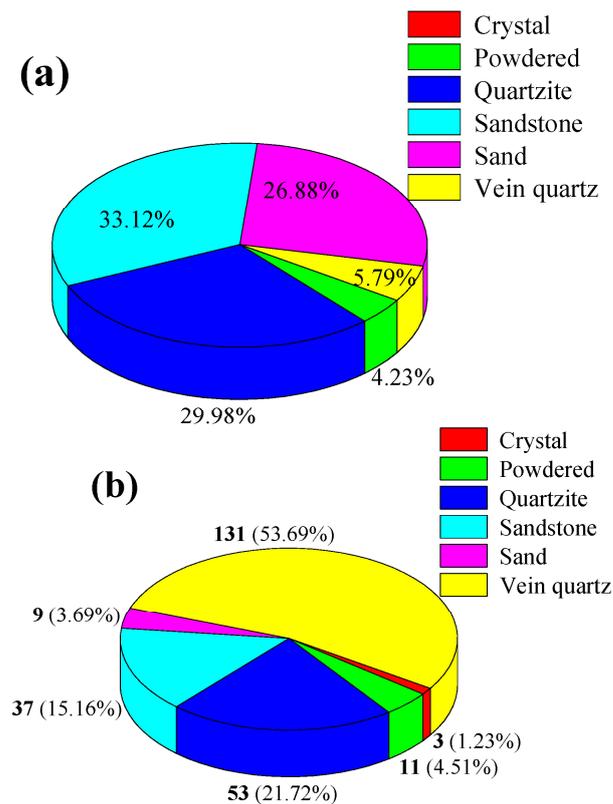


Figure 2. (a) The reserves of siliceous raw materials and (b) the number of deposits (with bold numerals) and their proportions (within parentheses) in Jiangxi Province, China.

2.2. Geological Origins of Quartz Deposits

Quartz minerals have a broad natural distribution, and the attributes of quartz deposits are shaped by geological factors. Currently, there are seven main industrial types of quartz deposits, namely natural crystal, quartz sandstone, quartzite, vein quartz, powder quartz, quartz sand and granite quartz. The primary silica raw material types in China, along with their fundamental characteristics, are detailed in Table 1 [9,10].

Natural crystals are favored for their high purity and transparency, making them the primary choice for producing high-purity quartz. However, their resource reserves are extremely limited, and mining conditions are unfavorable. Additionally, high-quality quartz resources of this kind are gradually depleting.

Vein quartz is characterized by its single mineral composition and high quartz content, with numerous mining locations. However, it generally has relatively small reserves and is challenging to mine. The primary reason for the mining difficulties is the irregular vein-like nature of vein quartz deposits.

Quartz sandstone typically consists of more than 95% quartz and siliceous clasts, with gangue minerals often including clay minerals like feldspar, kaolin, illite, and montmorillonite, and a low proportion of heavy minerals. Quartz sand primarily originates from modern lacustrine deposits in lakes and alluvial sediments along riverbanks. Due to its fine particle size, producing high-purity quartz sand at suitable grain sizes is challenging, resulting in limited reports of its use for high-end quartz products, both domestically and internationally. Taking Thrakon, a Greek company, as an example, they leverage the low impurity content of the Alada River quartz sand. After undergoing cleaning and drying processes, this sand serves as the primary component in construction mortar [11].

Table 1. The types and basic characteristics of siliceous raw material deposits in China.

Ore Type	Ore Genesis	Deposit Scale	Mineralogical Features	Application Areas	Resource Distribution/Extraction Status
Natural Crystal	Slow growth in crystal caves	Small	High purity, high transparency	Optical instruments, electronics	Low resource reserves, difficult to mine
Vein Quartz	Hydrothermal filling along fault fractures	Medium/small	Well-crystallized	Glass, metallurgy	Many mining locations, low reserves
Quartz Sandstone	Lacustrine deposition	Large/medium	Comprising intricate cementing materials	Glass, ceramics, building materials	Concentrated in southern China, easy to mine
Quartz Sand	Alluvial deposition	Large/medium	Lack of natural grain shape	Glass, construction, casting molds	Large reserves, favorable mining
Powder Quartz	Weathering residual	Large/medium	Extremely fine particle size	Metallurgy, glass, cement, ceramics	Found in Jiangxi, Guizhou, Hunan
Quartzite	Sedimentary deposits altered by metamorphism	Large/very large	Blocky structure	Refractories, silicon alloys, glass	Large reserves
Granite Quartz	Slow crystallization in deep magma	Large/very large	Large grains, higher impurity	Underdeveloped utilization	Widely distributed

Quartzite is a metamorphic rock formed from siliceous rocks through regional metamorphism or contact metamorphism induced by hydrothermal activity. It contains not only minerals like feldspar, mica, and clay minerals but also trace amounts of minerals such as tourmaline, hematite, and zircon. Natural powder quartz is a sedimentary weathering-type deposit formed through the weathering and disintegration of siliceous parent rocks. It is characterized by a high SiO₂ content but possesses an extremely fine grain size, with particle diameters typically falling within the range of 5–50 µm.

Granite quartz typically exhibits a relatively low SiO₂ content, where feldspar, mica, and kaolin collectively account for up to 80% of the total ore. Currently, the utilization of quartz in granite remains exceedingly limited. It is worth noting that some research suggests a direct proportionality between the concentration of impurities in quartz and its crystallization temperature. Quartz crystallized from granite melts with higher weathering levels tends to contain fewer structural impurities, as it forms at lower temperatures [12]. In comparison to other siliceous raw materials found in granite, coarse-grained pegmatite quartz offers greater potential for purification. Presently, only a select few mineral deposit types worldwide, including certain granitic pegmatites and hydrothermal quartz veins, have the capacity to produce high-purity quartz [13].

2.3. Impurities in Quartz Ores

The presence and quantity of impurities directly determine the ease or difficulty of quartz purification. Research indicates that siliceous raw materials contain various impurity minerals and elements, with the modes of occurrence and distribution patterns of these impurities being associated with the ore-forming processes [14]. For example, impurity distribution in layered hydrothermal vein quartz is typically highly uneven, while structural impurities in igneous and metamorphic quartz tend to have a more uniform distribution. In addition, Larsen et al. have identified a functional relationship between the concentration of structural impurities during quartz growth and the total impurity concentration in pegmatitic melts [14].

2.3.1. Impurity Elements

To examine the content and distribution of impurity elements within various types of quartz ores, five representative samples were selected, including vein quartz, powder quartz, quartzite, pegmatite quartz (referred to as pegmatite), and pegmatitic granite (referred to as granite) from Jiangxi Province. Based on the elements detected using X-ray fluorescence spectroscopy (XRF) of the original ores, chemical full-element analysis of the five types of ores was conducted using ICP-OES, ICP-MS, and high-frequency infrared carbon-sulfur analysis (HCS801A D548), as illustrated in Figure 3.

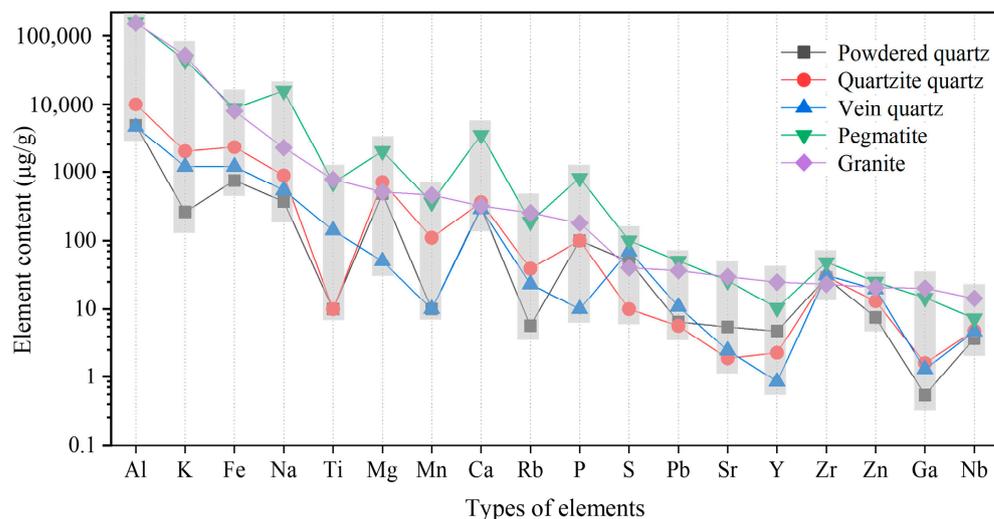


Figure 3. Comparison of impurity element content in different types of quartz ore.

Among the five selected types of quartz ores, the SiO_2 content ranks from highest to lowest as follows: powder quartz > vein quartz > quartzite > granite > pegmatite, with respective contents of 99.08%, 98.83%, 98.14%, 74.10%, and 73.46%. As depicted in Figure 3, the primary impurity elements in these quartz samples include Al, Fe, K, and Na, with trace amounts of Ti, Mg, Mn, Ca, and S. Additionally, microelements such as Pb, Sr, Y, Zr, Zn, Ga, and Nb are present. Notably, the Rb content is relatively high in all quartz types except for powder quartz, reaching a maximum of 189 $\mu\text{g/g}$. The distribution characteristics of these trace elements can provide valuable insights for the exploration of high-purity quartz deposits.

Upon analyzing the specific values of Al and K element contents in Figure 3, it is evident that there is a positive correlation between the Al and K contents in the five different quartz types, indicating that the impurity minerals in the original ores belong to the same class of aluminosilicate minerals. The Al content is also positively correlated with Fe, suggesting the presence of iron minerals or iron elements within the aluminosilicate minerals. Furthermore, Al dominates the high-purity quartz lattice, with lattice Al accounting for an average of 70% of the total metal impurities in high-purity quartz. The higher the purity, the greater this proportion, reaching a maximum of 91%. This is a primary indicator for assessing product quality and purification efficiency.

2.3.2. Coexisting Gangue Minerals

In quartz ores, coexisting gangue minerals can generally be divided into two categories: (i) loosely associated minerals, that often exhibit relatively intact mineral crystals and no chemical bonding with quartz crystals, such as feldspar, mica, garnet, zircon and ilmenite; (ii) the second category consists of companion mineral fragments that chemically and physically bond to the surface of quartz crystals, primarily comprising iron-bearing minerals and aluminum-bearing minerals, such as iron pyrite and iron olivine [15].

Four types of raw ores, including quartzite, vein quartz, pegmatite, and granite, were crushed, ground, and screened to particle sizes of 0.1–0.2 mm. Subsequently, a magnetic

separation process (with a magnetic field intensity of 1.2T) was applied to remove iron-bearing minerals. The pre-processed products were then subjected to mineral composition analysis using a BGRIMM Process Mineralogy Analyzer (BPMA, BGRIMM Technology Group, Beijing, China), which includes a TESCAN VEGA scanning electron microscope, a Bruker QUANTAX 200 dual-probe spectrometer, and automated analysis software for mineralogical processing (BMPA V2.0) [16]. The results are presented in Figure 4.

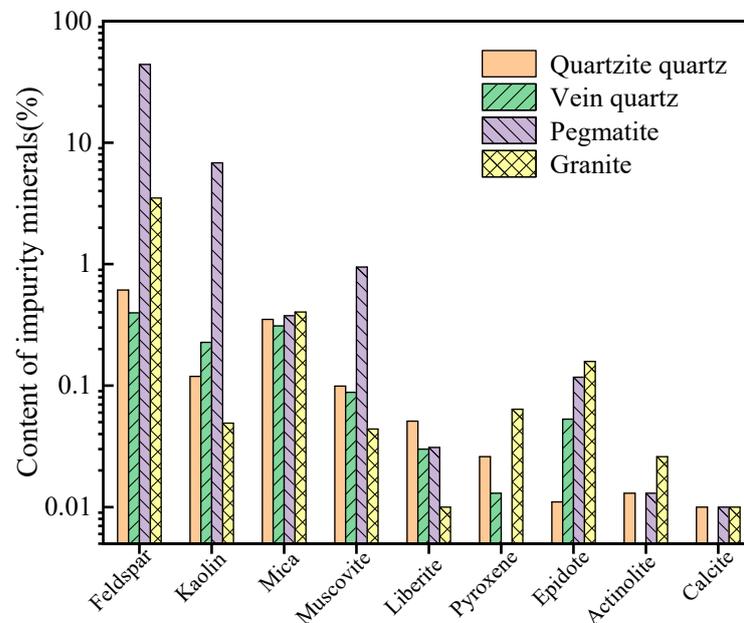


Figure 4. Comparison of impurity minerals content in different types of quartz ore.

As observed in Figure 4, the main impurity minerals include feldspar, amphibole, kaolin, and muscovite. Additionally, there are trace impurity minerals like liberite and epidote. It should be noted that the specific types of feldspar impurity minerals encompass potassium feldspar, sodium feldspar, albite, anorthoclase, and microcline. Similarly, the amphibole impurity minerals encompass riebeckite, blue amphibole, tremolite, and grunerite. The presence of minerals like actinolite, diopside, and augite, as well as calcite and rhodonite among trace impurities, depends on the type of ore.

2.3.3. Fluid Inclusions

Fluid inclusions are widely present in minerals, and their types and abundance depend on the petrogenetic environment and crystallographic variations of quartz minerals. Common types of fluid inclusions include gas phase, liquid phase, gas–liquid two-phase, and solid–liquid–gas three-phase inclusions, as illustrated in Figure 5 [17–19]. These fluid inclusions contain a significant quantity of impurities such as Na, K, Cl, and Ca, serving as the primary source of alkali metal impurities, while small molecular impurities are mainly found in gas and liquid phases. Fluid inclusions exhibit characteristics of fine-grain embedding, complex structural arrangements, diverse phase compositions, and high impurity element content. Therefore, the removal of impurity components constitutes crucial steps in most quartz raw material purification techniques. Schmidt-Mumm et al. suggest that the bursting of fluid inclusions can be categorized into the following processes: the expansion of micro-cracks, rupture of grain boundaries, trans-granular rupture, intragranular rupture, as well as the bursting of fluid inclusions [20]. It should be noted that the smaller the grain size of inclusions, the more challenging their removal becomes. For instance, a study conducted by Gawel et al. indicated that $-4\ \mu\text{m}$ fluid inclusions within quartz crystals remain stable even at temperatures as high as $800\ ^\circ\text{C}$ [21].

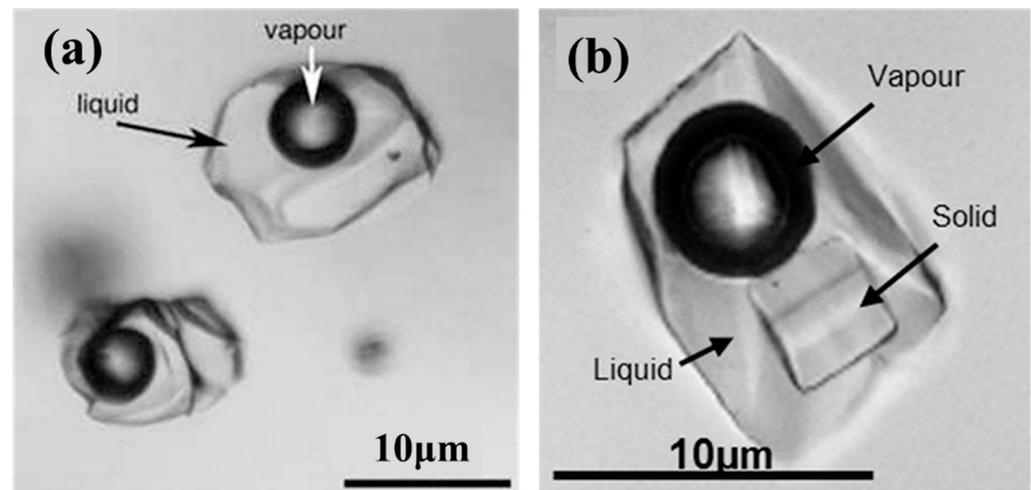


Figure 5. Photomicrograph of fluid inclusions in quartz (modified after Kendrick and Burnard [17] and Cai et al. [19]). (a) Gas–liquid two-phase inclusions; (b) solid–liquid–gas three-phase inclusions.

2.3.4. Mineral Inclusions

Mineral inclusions refer to minerals that coexist with quartz during the quartz crystallization process, either within the crystal lattice, along crystal fractures, or on crystal surfaces. They can also form during the recrystallization of quartz minerals under metamorphic conditions. These inclusions primarily comprise micron-scale particles ranging from 1 to 10 μm , sub-micron particles in the range of 0.1 to 1 μm , impurities at the nanometer scale, and atomic clusters smaller than 1 nm [22]. Presently, research has predominantly focused on blue igneous rock quartz; however, the prevalence of sub-micron and nanometer-scale solid inclusions in natural quartz remains uncertain [23,24]. Taking granite quartz as an example, the morphology of micron-scale mineral inclusions can be observed under a microscopy (ZEISS AxioScope 5), as illustrated in Figure 6.

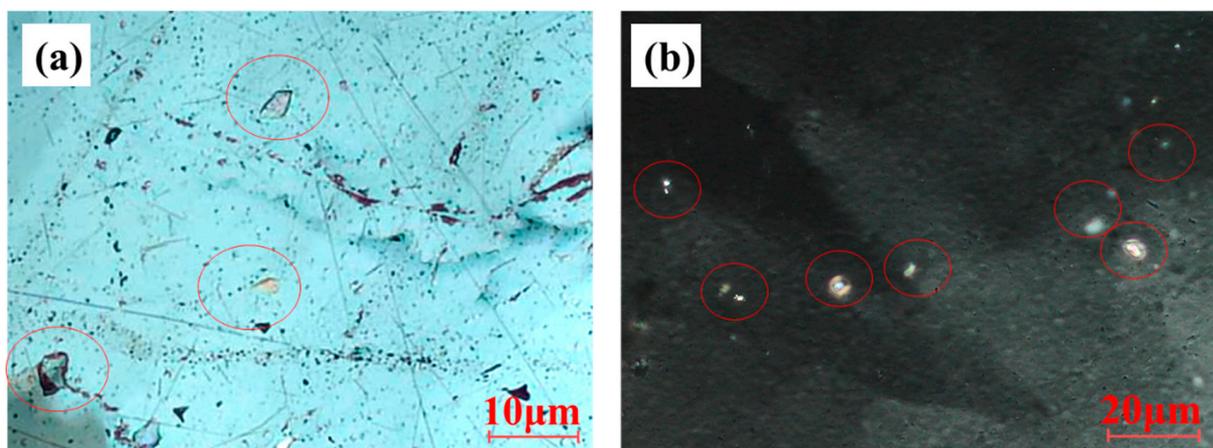


Figure 6. Micron-scale mineral inclusions in granite quartz. (a) Coarse-grained feldspar mineral inclusions (with a red circle) observed in plane-polarized light; (b) fine-grained mica mineral inclusions (with a red circle) observed in crossed-polarized light.

Given that mineral inclusions are predominantly situated within quartz mineral particles, their extraction poses a significant challenge. A primary contributing factor to this challenge is the strict particle size requirements in the production of high-end, high-purity quartz. For instance, products intended for photovoltaic materials demand a particle size range of 0.1 to 0.6 mm, making it unfeasible to overgrind the ore in an attempt to expose

mineral inclusions. Therefore, further development of removal processes for sub-micron and nanometer-scale solid inclusions within quartz is of utmost importance.

2.4. Structural Impurities in Quartz Minerals

2.4.1. Lattice Impurities

Structural impurities in quartz lattice can be primarily categorized into two major classes: (i) lattice substitution impurities, such as Al^{3+} , Fe^{3+} , B^{3+} , Ti^{4+} , and P^{5+} atoms that act as isomorphous substitutes for the Si^{4+} atoms within the silica tetrahedra; (ii) charge-compensating impurities. Due to internal charge imbalances in the lattice, ions such as Li^+ , K^+ , Na^+ , H^+ , and Fe^{2+} enter the lattice to form interstitial atoms, residing within the voids of the silica tetrahedral framework [6]. Furthermore, although germanium is naturally scarce; the common occurrence is the isovalent substitution of Ge^{4+} for Si^{4+} [25]. These impurities are also prone to diffusing both out of and into the quartz crystal. The specific combinations are illustrated in Figure 7 [26]. It is crucial to recognize that, owing to disparities in charges and ionic radii, only a restricted number of ions can effectively substitute for Si^{4+} in the crystal lattice or be integrated into interstitial positions. As for the majority of other trace impurity elements (e.g., Ca, Mg, Mn, Sr, Ga, Zr, and Rb), they tend to exhibit a higher concentration within fluid inclusions [25].

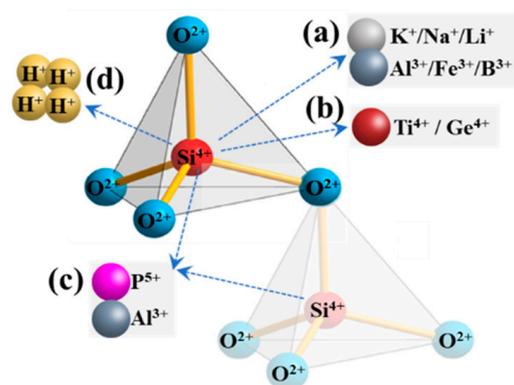


Figure 7. Diagram illustrating the forms of structural impurities in a quartz lattice. (a) Trivalent cation M^{3+} substituting Si^{4+} ; (b) tetravalent cation M^{4+} substituting Si^{4+} ; (c) different ion pairings replacing Si^{4+} ; (d) H^+ substituting Si^{4+} .

Unlike most other minerals, impurities in quartz crystals tend not to be uniformly distributed throughout the crystal. Within just a few micrometers, impurity concentrations can vary by an order of magnitude. Generally, in accordance with the principle of charge balance, the content of monovalent cations is similar to the content of trivalent cations. Recently, Götze et al. summarized impurity elements distributions in quartz of different origins: (i) Li^+ appears to be the dominant charge-compensating ion in igneous and pegmatite, preferentially bonding with structural channels to balance the charge of Al; (ii) the highest Ti contents are typically observed in volcanic and igneous rocks; (iii) the distribution of P is unstable, with slight enrichment observed in granite and pegmatite; (iv) Fe is predominantly present in the marginal zones or damaged areas of quartz crystals [25]. Due to the inherent difficulties in treating lattice impurities using conventional refining techniques, impurity removal processes are both intricate and costly. Therefore, quartz deposits with lower lattice impurity content hold greater potential for producing high-purity quartz.

2.4.2. Hydroxyl Impurities

Hydroxyl impurities are also the target for removal in the production process of ultra-high purity quartz. This is because, although hydrogen is not typically considered an impurity in natural quartz, it can combine with hydroxyl groups to form molecular water (approximately $10 \mu\text{g/g}$) [27]. This, in turn, reduces the fusion temperature of quartz and impacts its optical

properties. The distribution of hydroxyl groups in quartz is generally non-uniform, with the highest concentrations commonly found at the crystal center. Additionally, hydroxyl groups may be present at crystal interfaces, defects, or within inclusions [27].

Biró et al. conducted an analysis of hydroxyl concentrations in quartz phenocrysts from several rhyolites using non-polarized micro-FTIR and SEM cathodoluminescence imaging. Their results indicated that the hydroxyl content in volcanic quartz (approximately 2.8 $\mu\text{g/g}$) was lower than that in granite, metamorphic rock, and hydrothermal quartz [28]. Gawel et al. demonstrated that when heated to temperatures above 600 °C, liquid water at grain boundaries was removed. Further heating beyond 900 °C resulted in the vanishing of water existing in sealed fluid inclusions [29]; however, eliminating the remaining isolated surface -OH groups is quite challenging. Recently, Stalder conducted a comprehensive review on the incorporation of OH point defects in quartz, assessing their relevance to natural samples and geological processes. The study revealed that OH incorporation was influenced by the availability of trace metals (such as Li and Al) and protons. Furthermore, it was observed that pressure negatively affected the formation of OH defects, suggesting that the purest quartz formations likely occurred in the deep crust, close to the quartz/coesite transition [27]. In summary, when producing high-purity quartz, it is advisable to prioritize raw materials with low levels of structural and inclusion impurities.

3. Analyzing the Quartz Purification Process from a Mineralogical Perspective

3.1. Common Quartz Purification Techniques

Quartz purification methods vary based on the quartz's origin due to differences in crystallographic properties arising from diverse crystal structures [30]. Quartz minerals exhibit more than 15 distinct crystal structures, including tridymite, hexagonal quartz, coesite, stishovite, and amorphous quartz, among others. The theoretical transformation sequence of quartz at different temperatures includes α -quartz, β -quartz (at 573 °C), tridymite (at 870 °C), and α -cristobalite (at 1470 °C) [31]. Therefore, variations in the physical and chemical properties, impurity element content, optical characteristics, and other attributes of quartz contribute to differences in the efficacy of the purification process.

Zhang et al. investigated the impact of structural transformations in quartz crystals on the removal of iron impurities. Results showed that, after annealing at 900 °C for 4 h, the quartz crystal structure underwent a transformation, with a high content of β -quartz reaching 94.7% [32]. Subsequent quenching and solidification led to the formation of a structure favorable for the acid leaching of iron. Conversely, other research has indicated that the transformation of tridymite and hexagonal quartz does not provide substantial assistance in quartz purification [33].

From the perspective of quartz ore processing mineralogy, the preparation of high-purity quartz involves a combination of various purification methods due to the diversity and complexity of impurities present in the ore. This complexity adds intricacy to the processing flow. The typical processing sequence for high-purity quartz includes: (i) pre-treatment, which involves crushing, scrubbing, desliming, screening, and grinding; (ii) physical separation methods, including radiometric sorting, dense media separation, gravity separation, magnetic–electric separation, and flotation; (iii) chemical treatments, such as calcination–water quenching and leaching; (iv) advanced treatments, which encompass chlorination, roasting and vacuum refining [34]. The principles, functions, and characteristics of conventional purification methods are outlined in Table 2 [10]. Since the pre-treatment processes are relatively straightforward, research on purification methods primarily focuses on subsequent physical and chemical separation, as well as advanced treatments.

Table 2. Characteristics of common quartz purification methods.

Purification Method	Principle	Main Impurities Separated	Characteristics
Scrubbing	Mutual particle friction	Adhered fine clay and oxide films	Simple operation, low purification efficiency
Gravity Separation	Differences in mineral density	Heavy minerals like zircon, garnet, and epidote	Ore loss in the process
Magnetic Separation	Differences in mineral magnetism	Magnetic minerals such as magnetite, hematite, and pyrrhotite	Requires multiple stages of strong magnetic fields
Flotation	Differences in mineral surface properties	Silicate minerals like mica, feldspar, and iron minerals	Relies on the flotation reagent system
Calcination-Water Quenching	Volume expansion during quartz phase transition	Rupture and exposure of inclusion impurities	Enhances acid leaching purification
Leaching	Differential solubility in acids	Impurity elements like Fe, Al, Cr, Ti	Acidic nature with corrosive properties
Chlorination Roasting	Generation of chemical gradients with chlorine gas	Impurity elements within the lattice	Limited processing capacity, and gaseous chloride emissions

3.1.1. Flotation Separation

Flotation is a crucial step in removing impurity minerals. The primary impurity minerals are silicate minerals such as mica, feldspar, kaolin, and iron minerals. Based on the types of collectors, modifiers and the pH of the slurry environment, flotation methods can be broadly categorized into the following:

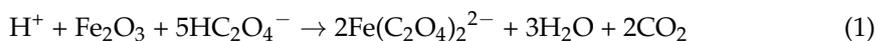
1. The “with fluoride and acid” method, involves the activation of feldspar using HF acid to enhance the differences in surface properties. Cationic collectors like dodecylamine are then employed to selectively capture the feldspar. However, it is important to note that the use of HF acid carries significant safety risks, and the wastewater generated during this process has a notable environmental impact [35].
2. The “without fluoride but with acid” method, entails floating feldspar under strongly acidic conditions, using a combination of cationic and anionic collectors such as dodecylamine and sodium oleate. Currently, this method represents a well-established industrial approach to quartz purification through flotation [36].
3. The “without fluoride and without acid” method involves floating feldspar under neutral or alkaline conditions. In a neutral setting, appropriate depressants are employed to remove anionic collectors from the quartz’s surface, inhibiting its flotation. In alkaline conditions, Mg^{2+} and Ca^{2+} ions serve as activators, while amine collectors or sodium alkyl sulfonates are used to selectively capture the quartz [37,38].

3.1.2. Acid Leaching

The effectiveness of acids in dissolving minerals varies significantly. Sulfuric acid works well for dissolving sulfide minerals and pyrite. Hydrochloric acid is efficient in dissolving calcite, dolomite, and galena. Nitric acid is capable of dissolving pyrite, siderite, and arsenopyrite. Hydrofluoric acid exhibits good solubility for silicate minerals like muscovite which is a major carrier of elements such as Al and K. Common mineral impurities found in quartz can undergo decomposition reactions in a mixed acid solution containing HF, with dissolution occurring in the following order from easy to difficult: spodumene > muscovite > calcite > albite > orthoclase > magnetite > pyrite > hematite [10].

Oxalic acid is the most widely employed organic acid in the acid leaching process. Its mechanism involves the formation of stable complexes with leached metal ions. Oxalic acid efficiently dissolves iron oxides, as depicted in Reaction (1) [39]. Apart from its strong chelating properties and reducing power, oxalic acid carries a lower risk of contaminating purified quartz after calcination compared to other leaching agents [40]. Sulfuric acid,

when used alone for iron removal, often demonstrates limited effectiveness due to the poor solubility of iron in minerals like mica. The concurrent application of oxalic acid substantially enhances iron removal efficiency [41].



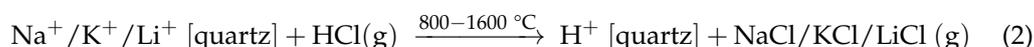
At present, research has primarily focused on eliminating iron elements, where the structural composition of iron-bearing minerals in quartz determines the ease or difficulty of iron removal. Studies have shown that goethite (FeOOH) dissolves more rapidly than hematite (Fe₂O₃), while minerals like alpha-hematite (α-Fe₂O₃) and gamma-hematite (γ-Fe₂O₃) are primarily dissolved through reduction reactions [40]. Similarly, the efficacy of iron removal varies significantly depending on the type of acid used. A study conducted by Zhang et al. showed that, with ultrasound assistance, phosphoric acid exhibited notably higher leaching efficiency for low-concentration iron impurities in quartz compared to other strong industrial acids like sulfuric acid, hydrochloric acid, nitric acid, and oxalic acid [42].

3.1.3. Calcination-Water Quenching

Calcination-water quenching is typically employed to reduce reaction time and reagent consumption by increasing the exposure probability of gangue minerals and disrupting their crystal structures. This method allows for the exposure of mineral inclusions and fluid inclusions in quartz due to the thermal stress, as well as the enrichment of elements such as Al, Li, Na, and K on the quartz surface during high-temperature phase transitions [43]. Due to its higher cost, this method is suitable for preparing 4N-grade high-purity quartz and is primarily applied in large-scale beneficiation plants. In addition, a study by Li et al. indicated that the addition of Na₂CO₃ during calcination reduced the phase transition temperature from α-quartz to β-quartz, providing more pathways for the migration of impurity elements during the subsequent leaching process [26].

3.1.4. Chlorination Roasting

Chlorination roasting takes place at temperatures below the melting point of quartz (1723 °C), where impurities within the quartz react with chlorinating agents, transforming into chlorides and subsequently volatilizing [31]. Depending on the type of chlorinating agent employed, chlorination roasting can be categorized into solid-state and gaseous chlorination roasting. Common chlorinating agents for solid-state chlorination roasting include NaCl, CaCl₂, and NH₄Cl, while gaseous chlorination roasting typically employs Cl₂ and HCl. Kenneth et al. revealed that alkali metal impurities underwent chemical reactions in an HCl atmosphere during roasting, as illustrated in Equation (2) [44].



Although chlorination roasting is effective in removing impurity elements such as Na, K, Fe, and Li from the quartz lattice, it is associated with emissions of gaseous chlorides, posing certain risks and environmental pollution concerns. Additionally, this process demands high-quality feedstock, typically requiring quartz with a SiO₂ purity exceeding 99.9% after conventional purification methods. Currently, only several foreign industrial applications have been reported, such as the United States' Unimin Corporation, with limited reports in China.

3.2. Current Status of Research on Quartz Purification Processes

Currently, in China, high-purity quartz materials predominantly utilize natural crystals. However, as the supply of crystal resources diminishes, research into purification using other quartz mineral resources is gradually advancing. In order to compare the purification potential of different siliceous raw materials, this study exclusively focuses on purification research involving the raw quartz ore (unprocessed quartz ore). Research results on the purification processes of various types of quartz ore are summarized in Table 3.

Table 3. Research results on processing of several typical siliceous raw materials for the preparation of high-purity quartz.

Types of Ores	Location	SiO ₂ of Raw Ore/%	Feed Size/mm	Purification Process	SiO ₂ of Purified Product/%	References
Vein quartz	Anhui Dabie Mountain	99.06	0.074–0.1	Crushing–grinding–calcination–water quenching–flotation–leaching	>99.99	[45]
	Sichuan province	99.95	<0.38	Crushing–calcination–water quenching–leaching	>99.99	[46]
	Anhui province	99.67	<0.29	Calcination–water quenching–flotation–leaching–washing	>99.9	[47]
	Sichuan province	99.96	<0.1	Crushing–screening–magnetic separation–flotation–high–temperature high–pressure leaching	>99.99	[48]
Quartz sandstone	Sichuan Muchuan county	93.42	0.1–0.2	Crushing–scrubbing–grinding–magnetic separation–leaching	>99.9	[49]
	Sichuan Leshan	97.08	<0.074	Crushing–grinding–washing–leaching–roasting–water quenching secondary leaching	>99	[50]
	Ningxia Helanshan	98.48	<0.096	Calcination–water quenching–grinding scrubbing–magnetic separation–leaching	>99.9	[51]
Quartzite	Jiangxi Tonggu	97.44	0.106–0.425	Crushing–screening–grinding–magnetic separation–leaching	>99	[1]
Powder quartz	Jiangxi Province	97.90	<0.04	Screening–magnetic separation–flotation–leaching–calcination	>99.9	[52]
Granite/pegmatite	Gansu Akse County	Quartz content ~25%	0.096–0.21	Crushing–roasting–water quenching–magnetic separation–color sorting–high–temperature high–pressure leaching–flotation–heavy liquid separation–high–temperature chlorination–high–temperature oxidation	>99.99	[53]
	Xinjiang Altai	84.45	<0.425	Crushing–gravity separation–magnetic separation–flotation–calcination–water quenching–leaching	>99.99	[54]

The SiO₂ content in quartz ores varies significantly depending on their origin, with a rough descending order as follows: crystal quartz > vein quartz > powder quartz > quartzite > quartz sandstone > pegmatite/granite. Quartzite, vein quartz, quartz sandstone, and powder quartz exhibit SiO₂ content exceeding 93%, with some high-quality vein quartz and powder quartz containing over 99% SiO₂. Granite or pegmatite quartz, while capable of reaching SiO₂ content of over 80%, generally contains lower proportions of quartz minerals within the ore, approximately around 20%–30%.

Quartzite, due to Al-Si entanglement resulting from magmatic separation or alteration processes, tends to have higher levels of mineral inclusions and isomorphous impurities. These fine-grained impurity minerals present at mineral interfaces and within the ore cannot be exposed during crushing and grinding processes and are thus challenging to remove during conventional leaching, making it difficult to achieve 3N purity levels. As a result, these common deposits are either processed into low-end products or, when increasing grinding fineness, they come with significant compromises in application. One distinctive feature of natural powder quartz is its extremely fine particle size, enabling cost reduction in the purification process by eliminating the need for crushing and grinding. However, the drawback is that powder quartz's particle size is often too fine to meet the granularity requirements of high-end high-purity quartz products.

In recent years, granite or pegmatite quartz has gained attention. In the Henan Province, the Nonferrous Metal Geological Bureau discovered a granitic pegmatite, similar to the Spruce Pine pegmatitic granite in North Carolina, USA. Through a processing method involving roasting, water quenching, crushing, grinding, flotation, and acid leaching, it becomes possible to obtain 4N high-purity quartz [55]. Researchers like Tian et al. have also successfully produced 4N or higher high-purity quartz sand from natural pegmatitic granite through processes including crushing, grinding, magnetic separation, color sorting, high-temperature and high-pressure acid washing, flotation, heavy liquid separation, high-temperature chlorination, and high-temperature oxidation [53]. Nonetheless, there exists considerable disparity in the quality of granite, coupled with poor homogeneity, which presents formidable challenges in terms of ore selection and impurity elimination. At present, there are no mines dedicated to producing high-purity quartz from granite quartz in China. Instead, this type of quartz is mainly utilized as associated mineral resources or processed as tailings.

In summary, the diversity in types, occurrences, and distribution characteristics of quartz impurities result in varying purification processes for different types of quartz mineral resources. Even within the same type and different locations of ores, the purification processes can differ significantly, posing substantial challenges to the development of purification techniques.

4. Challenges of Quartz Purification Technology

4.1. Selection and Evaluation of Purification Materials

In the past, high-purity crystal quartz, characterized by low hydroxyl content and minimal inclusions, was the primary choice for processing in the production of high-purity quartz. This process was relatively straightforward, but it placed a significant reliance on the quality of the raw material. However, with the gradual depletion of natural crystal-grade quartz resources, there is now an increasing urgency to use common quartz ores for high-purity quartz production.

Currently, the selection of high-purity quartz raw materials often involves a significant degree of arbitrariness, driven by the misconception that SiO₂ purity level is the most crucial factor in high-purity quartz production. In reality, the impurity element content in the raw material does not always directly correlate with the potential for purification in high-purity quartz. Take granite quartz as an example, where the primary minerals in the rock are quartz, feldspar, and mica. Although the quartz content might be relatively low (about 20%–30%), the crystalline quartz minerals in granite often contain very few structural impurities, potentially rendering it with higher purification potential [12].

In addition to the impurity content, the distribution of impurities is of equal importance. The distribution of impurities in quartz ores is linked to the rock-forming process. For instance, impurity distribution in hydrothermal vein quartz is typically highly uneven, while structural impurities in igneous and metamorphic quartz tend to be more evenly distributed [14]. Larsen et al. found that the concentration of structural impurities during quartz growth was related to the total impurity concentration in pegmatitic melts, providing evidence for the aforementioned viewpoint [14]. Therefore, the origin of the ore determines the mode of occurrence and distribution patterns of impurities, while the mineralogical characteristics of the ore play a pivotal constraint in quartz purification, determining the upper limit of quartz purity that can be achieved. Hence, the lack of a robust foundation for assessing and selecting high-purity quartz raw materials remains a fundamental challenge in the development of the high-purity quartz industry.

4.2. The Challenges in Purification Technology

4.2.1. The Challenge of Complete Quartz Monomer Liberation

Given the stringent size requirements for high-purity quartz products, such as the need for photovoltaic glass sand to fall within the 0.1–0.6 mm range, the minimum threshold for product crushing and grinding is set at 0.1 mm. If quartz cannot achieve complete monomer liberation at this size or fail to meet the required liberation degree, it will pose significant challenges in subsequent ore selection processes. However, many existing studies have not taken into account these size requirements, often grinding quartz to below 0.1 mm (as seen in Table 3) in an attempt to enhance monomer liberation.

As an illustration, in the case of four different types of quartz ores, namely quartzite, vein quartz, pegmatite, and granite, a conventional crushing and grinding technique (using jaw crushers and ceramic ball mills) was employed to reduce the raw ore to the size range of 0.1–0.2 mm. The degree of liberation was then assessed using the BGRIMM Process Mineralogy Analyzer (BPMA), and the results are presented in Figure 8. From Figure 8, it is evident that the monomer liberation levels for the four different types of quartz ores are generally not high, and there are notable disparities among them. Granite displays the highest liberation degree, reaching up to 95%, while vein quartz exhibits the lowest disintegration, at just 80%. This can be attributed to incomplete alteration processes in the geological origin of vein quartz, resulting in residual host rock and intergrown quartz minerals.

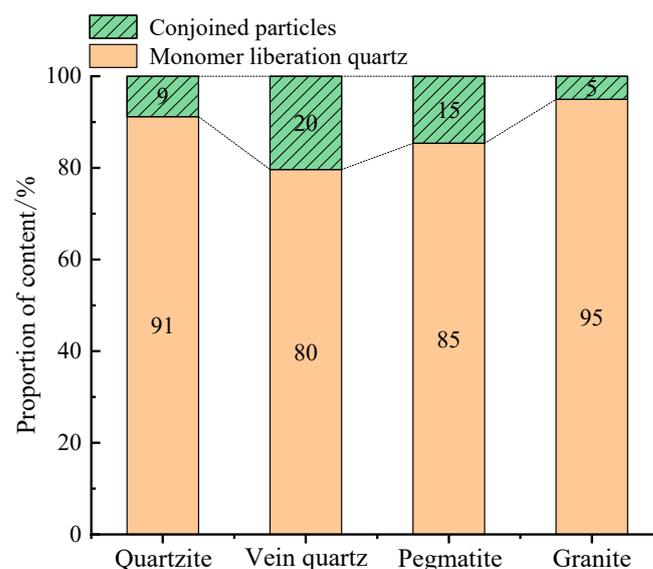


Figure 8. Degree of liberation to various quartz ores of different origins via crushing and grinding (particle size: 0.1~0.2 mm).

4.2.2. Acid Consumption and Pollution in the Leaching Process

Acid leaching is a crucial step in removing impurity elements, and its effectiveness depends largely on the type of acid. Common inorganic acids include HF, H₂SO₄, HCl, HNO₃, H₃PO₄, and HClO₄, while organic acids comprise ethylenediaminetetraacetic acid (EDTA), citric acid, thioacetic acid, and oxalic acid, among others, often combined in specific ratios [56,57]. Lee et al. purified quartz that had undergone flotation, heavy medium separation, and magnetic separation using different types of inorganic acids and found that the removal capacity of various acids for impurities in quartz followed a sequence from strong to weak: HCl/HF (2.5%) > HNO₃/HF (1%) > aqua regia > oxalic acid (0.2 M) > oxalic acid (0.2 M) [58]. Using HCl/HF (2.5%) as the leaching agent, the removal rates for major and trace impurities both exceeded 65%, although this acid combination displayed less effectiveness in removing calcium.

Research has shown that the use of HF is advantageous for removing major impurity minerals such as feldspar, mica, and kaolin from quartz [59]. Zhou et al. indicated that, after acid leaching at 120 °C and an HF-to-water ratio between 0.4 to 0.5, the purity of quartz could meet the technical requirements for mid-to-high-grade quartz glass [60]. However, the use of fluoride reagents, especially HF, unavoidably results in environmental pollution.

In recent years, researchers have proposed a series of methods to enhance the leaching process, including microwave-assisted leaching, which accelerates the dissolution of gas-liquid inclusions but consumes significant energy [61]; multi-thermal shock leaching, which increases the density of mineral surface fractures but involves complex operations [62]; hot-press leaching, which offers high efficiency but requires rigorous conditions [8]; and ultrasound-assisted leaching, known for its ability to accelerate reaction rates and reduce acid consumption, but has limited processing capacity and lacks scalability [63].

4.2.3. Complexity of the Purification Process

From a purification process perspective, whether involving physical, chemical, or advanced treatment methods, a common drawback of various methods is their ability to remove specific types of impurity elements or impurity minerals only. This drawback inevitably leads to lengthy process flows in the preparation of high-purity quartz. The lengthy process flow has two consequences: (i) high operating costs; and (ii) unstable operation and uncertain product quality.

For instance, Du et al. focused on vein quartz from Donghai County, using a process involving roasting, water quenching, screening, magnetic separation, flotation, acid leaching, washing, and high-temperature roasting to produce 4N high-purity quartz, highlighting the importance of screening and high-temperature roasting as essential steps in quartz purification [64]. In contrast, Yuan et al. used vein quartz from Huoshan County, Anhui Province, and employed a process of roasting, water quenching, flotation, acid leaching, and washing to achieve 4N level, suggesting that screening and high-temperature treatment have less noticeable effects on removing impurity elements from quartz [47].

Additionally, various purification processes have been proposed for vein quartz, including: (i) magnetic separation-reverse flotation-high-temperature high-pressure leaching; (ii) shaking table-positive flotation-reverse flotation; and (iii) screening-magnetic separation-flotation-water washing. All these approaches achieved purity levels exceeding 99.9% for quartz concentrates [22,48,65]. Nevertheless, these methods suffer from challenges like low purification efficiency, intricate processes, strict conditions, and unstable product quality, restricting their industrial applicability.

In summary, China possesses abundant quartz mineral resources, but its development and utilization methods remain relatively rudimentary. These limitations manifest in small-scale production and low resource utilization rates. Moreover, there is a common occurrence of using high-quality quartz raw materials for low-quality applications. Some high-quality quartz materials are used for ordinary glass raw materials, cement ingredients, or even basic construction stone, resulting in low technical content. In certain regions, these

superior quartz raw materials are even sold as raw ores, leading to a substantial outflow of these resources.

In the early 1970s, international endeavors commenced to investigate the utilization of common siliceous ores as a substitute for natural crystals in the production of high-purity quartz sand. During the 1980s, the U.S.-based PPCC company successfully purified 4N grade high-purity quartz sand derived from granite in the Foxdale region of the United Kingdom [10]. In the 1990s, Japan initiated the separation and processing of high-purity quartz sand sourced from fine-grained pegmatite. Concurrently, Germany and Russia directed their efforts towards vein quartz and quartzite. In recent years, the U.S.-based Unimin company has achieved the purification of 4N~5N high-purity quartz sand from granite in the Spruce Pine region of North Carolina. This is characterized by superior quartz resources, extensive scale, elevated purification standards, and stable product quality [61,66]. Notably, due to the strategic significance of high-purity quartz, the technology for manufacturing premium products abroad is rigorously safeguarded, resulting in limited reports on the entire process of purifying and processing from quartz ore to high-purity quartz sand products.

In contrast to China, foreign nations possess notable advantages in advanced processing techniques such as high-pressure chlorination roasting, electrical pulse fragmentation, and microwave heating, facilitating the removal of coexisting minerals and structural impurities. Presently, Unimin in the United States may stand as the sole entity to have achieved industrial application of chlorination roasting in the purification of high-purity quartz. Martello et al. proposed the application of electrical pulse fragmentation for refining quartz raw materials to eliminate trace mineral impurities, demonstrating enhanced monomer liberation efficiency of quartz grains, albeit with the drawback of substantial equipment investment [67]. Furthermore, Buttress et al. introduced a methodology for producing high-purity quartz utilizing microwave pretreatment to fracture microfluidic inclusions. The methodology capitalizes on the explosive rupture of fluid inclusions in quartz induced by microwave heating. When coupled with high-gradient magnetic separation and acid leaching processes, this approach reduces impurity content from 158 µg/g to 30 µg/g [61].

In China, traditional physical beneficiation and chemical methods for preparing 3N grade high-purity quartz have seen numerous applications. However, the technology for producing 4N to 5N grade high-purity quartz remains underdeveloped. With the ongoing growth of the new-generation information industry, there are increasingly strict requirements for the types and levels of impurities in high-purity quartz mineral products, further constraining the utilization process of high-purity quartz resources. Therefore, exploring intensified techniques for impurity removal in quartz and researching clean, efficient, and short-process purification methods are critical directions to advance the industrial application of high-purity quartz derived from natural siliceous mineral resources.

5. Conclusions and Outlook

From a resource perspective, China possesses abundant reserves of natural siliceous mineral resources, with quartz sandstone, quartzite, and quartz sand accounting for approximately 90% of the total resource reserves. However, mineral deposits capable of producing high-purity quartz are exceedingly rare. Currently, the only siliceous raw material used in industrial high-purity quartz production is crystal quartz. The formation of high-quality natural quartz minerals is determined by specific geological environments, and it can only occur under particular physical and chemical conditions. Thus, intensifying exploration efforts to discover high-quality siliceous raw materials for high-purity quartz production is the key to addressing resource limitations.

From a mineralogical perspective, the purification potential of quartz is inherently linked to its deposit type, ore genesis, and mineral characteristics. The quality of quartz is not solely determined by the content of impurity elements in the raw ores but is more significantly related to the form of impurity occurrences, a feature primarily determined by the mineralogical traits of quartz itself. However, the current lack of criteria for the evalua-

tion and selection of high-purity quartz raw materials is a fundamental issue that hinders the development of the high-purity quartz industry. Therefore, conducting further research into the genetic characteristics of siliceous raw material deposits, ores, and minerals, and establishing a scientific and effective method for evaluating the purification potential of quartz ores, holds significant theoretical and practical importance for the selection of quartz purification materials.

From a purification process perspective, whether involving physical, chemical, or advanced treatments, a common drawback of various methods is their ability to remove specific types of impurity elements or impurity minerals only. This limitation inevitably results in lengthy process flows for the preparation of high-purity quartz. Challenges such as the difficult complete disintegration of quartz monomers, high acid consumption in the leaching process, and the complexity of the purification process are common issues in existing purification technologies. Different types of impurities require different treatment methods. Consequently, it is crucial to develop purification processes based on the occurrence status and characteristics of impurities in quartz ores, taking into account the mineralogical properties of siliceous raw materials. Therefore, considering the mineralogical properties of siliceous raw materials, the integration of exploration and purification processing for quartz deposits offers a promising avenue for the future. Knowledge-based design and the development of economically efficient and environmentally friendly short-process technologies may hold the key to this endeavor.

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