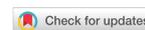


Review

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Recent advances in the marketing, impurity characterization and purification of quartz

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Abstract

Due to its stable physical and chemical properties and its abundance in nature, quartz is widely employed in industrial and high-tech applications. However, the presence of diverse types and states of impurities in quartz ores from different geological formations poses a challenge in the process of purifying high-purity quartz, leading to wastage of raw materials and escalated costs. This study presents the socio-economic applications of quartz, scrutinizes the formation and separation mechanisms of impurities in quartz ores from a mineralogical perspective, examines the obstacles faced in quartz purification, explains the current state of development, and provides a technical summary of quartz purification. The analysis reveals that lattice impurity elements and various types of inclusion impurities are the principal factors affecting the purity of quartz. Various green separation techniques are applied based on the composition of the quartz minerals and the state of the impurities. Standard practices may involve physical pre-treatment such as scrubbing, ultrasonic crushing, and electromagnetic pulse cracking, followed by rough cleaning through color separation, superconducting high gradient magnetic separation, and flotation, and chemical pre-treatment (high-temperature or microwave roasting with chloride doping, and ammonium sulfate thermal crushing combined with water quenching to remove gas-liquid inclusions from quartz minerals). Finally, finishing processes such as fluorine-free and catalytic hot-pressure acid leaching or microbiological purification treatment with filamentous or *Aspergillus* fungi are used to obtain high-purity silica sand with an anticipated purity of about 99.99%.

Keywords: Quartz, inclusions, purification, impurity separation, application



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INTRODUCTION

Quartz has attained a prominent status as a pivotal high-tech material, finding extensive employment across a diverse spectrum of fields encompassing high-purity glass, refractory materials, solar energy, computers, optical fibers, aerospace, and medical applications^[1,2]. In select countries, quartz also assumes vital roles in the realms of cosmetics, automotive components such as car wheels, as well as zeolites and adsorbents^[3]. Quartz typically exhibits a colorless or white and transparent appearance, possessing a density of approximately 2.65 g/cm³ and a Mohs hardness rating of 7. Its principal constituent is silica, characterized by a melting point ranging from approximately 1,710 to 1,756 °C. Notably, quartz manifests solubility solely in hydrofluoric acid (HF) while displaying only slight solubility in potassium hydroxide (KOH)^[4].

The era of information and the rapid advancements in technology have led to increasing demands for high-purity quartz. The high-tech industry specifically requires quartz with a minimum SiO₂ content of 99.9%, and in some cases even surpassing 99.99%. However, the reserves of high-purity quartz derived from natural crystal ores are depleting, rendering them not only scarce but also economically inefficient due to their high price. Consequently, the exploration of low-grade quartz ores has gained significant attention in order to meet the substantial market demand. The primary impurity elements found in quartz include aluminum (Al), iron (Fe), boron (B), lithium (Li), sodium (Na), potassium (K), and calcium (Ca). In high-tech applications, stringent purity requirements dictate that the impurity levels in quartz should generally be below 20 ppm^[5]. When the impurity concentration in quartz ore falls below 50 µg/g, the prevailing impurity elements are primarily Al, Fe, and B. Purification processes for quartz typically aim to achieve ferric oxide (Fe₂O₃) content below 15 ppm and aluminum oxide (Al₂O₃) content below 300 ppm^[6].

Traditional impurity removal methods mainly use a combination of physical and chemical methods to remove impurities, including the use of HF in acid leaching, which is effective but extremely harmful to human health and the environment, and HF can also cause loss of ore resources^[7,8]. Strong acids such as hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) are also used but are also very harmful to the environment. In the context of optical glass, stringent requirements exist for minimizing the presence of Fe impurities. Consequently, researchers commonly employ a combination of techniques, including roasting, magnetic separation, and acid leaching, to eliminate Fe^[9,10]. For instance, Lin *et al.* achieved a remarkable 98% reduction in Fe impurity content through a process involving roasting at 900 °C followed by leaching with H₂SO₄ and ammonium chloride (NH₄Cl) at 250 °C^[11]. Similarly, Yang *et al.* successfully enhanced the SiO₂ purity from 99.6828% to 99.9047% by employing a calcination pre-treatment in conjunction with ultrasonic-assisted leaching^[12]. Furthermore, Dal Martello *et al.* also used electrochemical methods to further purify quartz, creating conditions for high-quality monocrystalline silicon extraction^[13].

Through a mineralogical lens, researchers have investigated the mechanism of removing impurities from quartz, unveiling the superiority of organic acids over inorganic acids in terms of efficiency, cost-effectiveness, and environmental impact. In the context of Fe removal, Zhong *et al.* employed organic acids such as oxalic acid and citric acid as leaching agents, demonstrating their capability to enhance the efficiency of impurity elimination^[14]. In addition, Šuba *et al.* implemented a combination of bioleaching, washing, and electromagnetic separation to target Fe impurities existing as attachments and within the lattice structure^[9]. This approach proved successful in removing most Fe impurities. Zhang *et al.* utilized phosphoric acid (H₃PO₄) to eliminate Fe from quartz minerals, achieving an optimal leaching rate of 77.1%, surpassing alternative methods by approximately 30% in terms of leaching efficiency^[15].

Distinct quartz products require varying levels of quartz purity, a characteristic contingent upon the nature of impurities and the presence of inclusions within the quartz matrix. In the initial stage, the minerals'

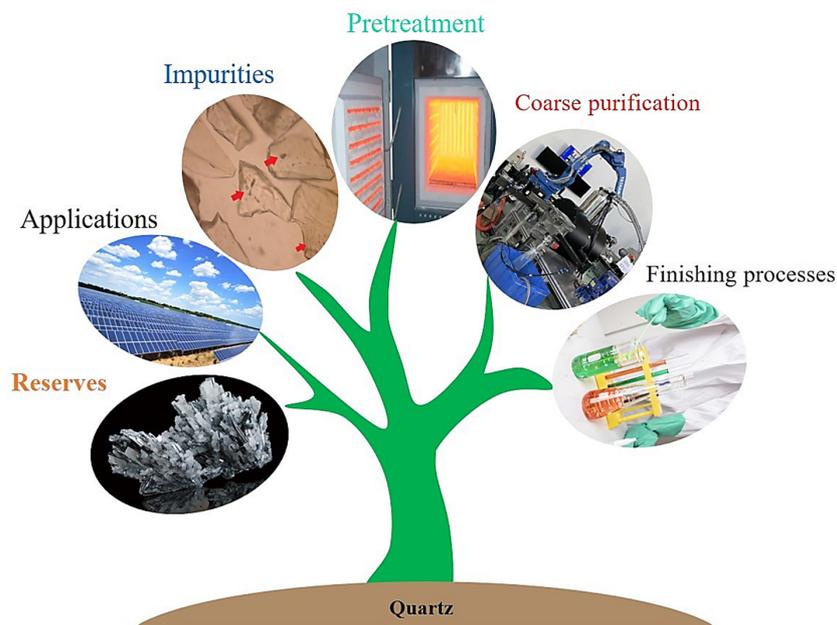


Figure 1. Main structure of the study.

impurity elements are meticulously characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) equipment before beginning the purification process. In the subsequent stage, the impurity composition is taken into account, and appropriate physical pre-treatment and crude purification techniques are adopted. Lastly, high-purity quartz is produced from ordinary quartz via final purification by means of hydrometallurgy or microbial leaching. Tailored purification processes are adopted, considering the specific impurity characteristics of the quartz, thereby enhancing cost-efficiency and overall effectiveness while attaining high-purity quartz. Nonetheless, it is important to acknowledge that although microbial leaching exhibits economic and environmentally friendly traits, its industrial implementation has been limited due to prolonged leaching cycles, lower efficiency, and inferior leach purity compared to wet leaching methods^[16-18]. [Figure 1](#) illustrates the main elements of this study.

RESERVES AND DISTRIBUTION OF QUARTZ RESOURCES

China boasts ample reserves of quartz ore, encompassing various types such as quartz sandstone, vein quartz (crystal), quartzite, and natural quartz sand^[19]. However, China's quartz reserves are mainly small to medium in size and are not concentrated, with the highest proportion in the northwest, as shown in [Figure 2A](#)^[19].

Brazil is the world's largest producer of high-purity silica sand, with impressive reserves of 21 million tons, which represent 29% of the world's total known reserves. The United States follows closely behind Brazil in vein quartz reserves, as illustrated in [Figure 2B](#). In the United States, which possesses 25% of the world's overall reserves, granite quartz takes precedence as the primary quartz variant. Canada, on the other hand, recorded quartz reserves amounting to ten million tons in 2019, constituting 13% of global reserves, with vein quartz emerging as the third most abundant type^[20].

Between 2015 and 2022, China's production, imports, and demand for quartz were all increasing. The corresponding fluctuations in these three aspects over the course of five years are graphically represented in [Figure 2C](#). The figure visually illustrates the rapid growth observed in China's quartz production and

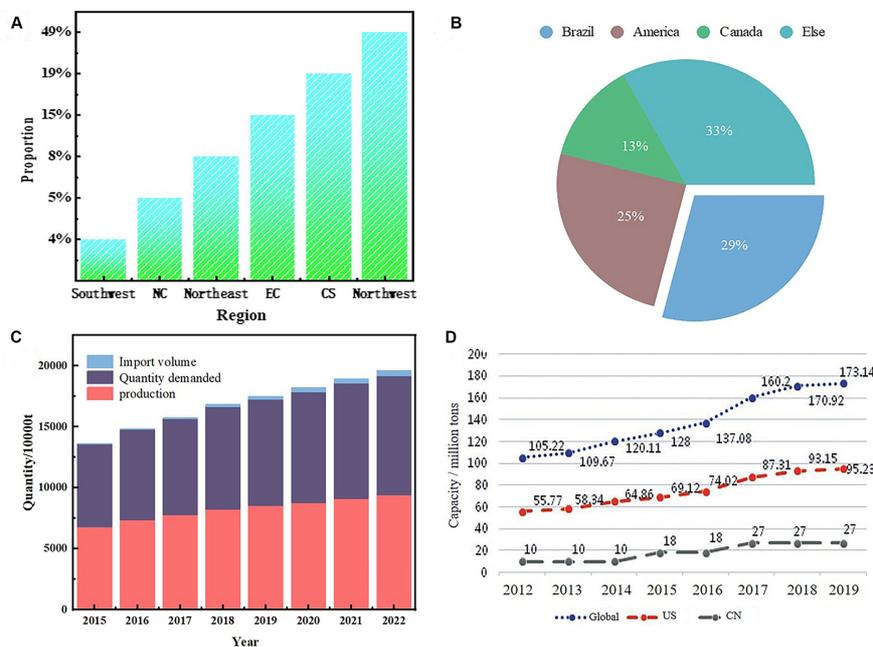


Figure 2. (A) The distribution of quartz ore reserves in China; (B) The global quartz ore reserves; (C) The change of quartz in various fields in China (<https://gonyn.com>); (D) The global and major countries' high-purity quartz sand production capacity.

market demand over the aforementioned period, alongside a surge in imports, primarily comprising high-purity quartz sand. In 2019, China's import volume of ultra-high-purity quartz exceeded its exports by a factor of 109, with imports of high-purity quartz (SiO_2 content surpassing 99.99%) reaching an impressive 14.45 million tons, valued at approximately USD 9,000 per ton^[21]. Figure 2D shows the global production capacity of high-purity quartz of 173.14 million tons per year in the year 2019. Presently, high-purity quartz is primarily derived from crystal (both primary and secondary) and vein quartz. The utilization of high-grade crystal ensures the production of high-purity quartz characterized by minimal impurities, enhanced purity, and transparency, with alpha quartz (α -quartz) constituting the primary component. However, the extraction of high-purity quartz from natural crystal raw materials proves to be a costly endeavor. In order to achieve resource recycling and reduce the production costs associated with high-purity quartz, researchers across various nations are increasingly focusing on exploring the purification potential of quartz and other mineral waste as alternative raw materials^[22].

CONSUMPTION STRUCTURE OF QUARTZ PRODUCTS IN THE MARKET

The current market classification of quartz is based on its purity levels, categorized as high-purity quartz with SiO_2 content ranging from 3 to 5 N and ultra-high-purity quartz with SiO_2 content ranging from 6 to 7 N. N indicates purity, 1 N indicates SiO_2 content greater than 90%, 2 N indicates SiO_2 content greater than 99%, and 3 N indicates SiO_2 content greater than 99.9%^[23]. Table 1, sourced from Richard Flook, presents the SiO_2 content requirements for various grades of quartz used in different products. It is evident from the table that as the SiO_2 content of quartz increases, the impurity content decreases, but the annual production volume decreases while the price increases. The recovery of raw silicon from mineral waste has a positive environmental impact, reducing CO_2 emissions and promoting energy savings while also indirectly generating economic value^[24]. SiO_2 used in the photovoltaic industry has strict impurity requirements, particularly for Fe and Ni, as these impurities reduce the photoelectric conversion efficiency^[25,26].

Table 1. Minimum SiO₂ content requirements for each grade of quartz products^[3]

Applications	Min. SiO ₂ (%)	Impurity elements (max %)	Impurity elements (max. ppm)	Market demand (million t/year)	Market price (USD/t)
Semiconductors, optical glass, and LCDs	99.8	0.2	2,000	2	150
Clear glass sand	99.5	0.5	5,000	> 70	30
Low-grade, high-purity quartz	99.95	0.05	500	0.75	300
Medium-grade, high-purity quartz	99.99	0.01	100	0.25	500
High-grade, high-purity quartz	99.997	0.003	30	< 0.1	1,000-5,000

"High-grade" high-purity quartz, impurities < 30 ppm, standard high-purity material from Unimin (Iota). Note 1: Specific requirements may be limited by other applications. For example, Fe₂O₃ < 100 ppm for float glass and Fe₂O₃ < 40 ppm for low-iron float glass. Note 2: Typically, "high-purity" quartz has Fe₂O₃ < 15 ppm, Al₂O₃ < 300 ppm, and alkaline earths and alkaline earth oxides < 150 ppm. Note 3: In some practices, Al₂O₃ can replace some SiO₂, such as up to 1.5% Al₂O₃ in float glass. Note 4: Threshold limits may vary depending on the composition of the other raw materials used in the application. LCD: Liquid crystal display.

The SiO₂ content of high-purity quartz ranges from 99.5 % to 99.99 %. This class of quartz is often used in the semiconductor, optoelectronics, and healthcare industries and for laboratory equipment. Raw materials with a purity of more than 99.99 % are used in the production of laser and optical components. Furthermore, ultra-high-purity quartz, with a purity range of 99.995% to 99.9999%, plays a critical role in photovoltaic power generation and in the semiconductor industry^[27]. The transparent light bulbs used in UV water purification and the silica glass used in the manufacture of solar-grade crucibles require not only high purity but also high light transmission and radiation resistance^[28-30]. The high-purity quartz market has experienced growth in recent years, primarily driven by the rising demand from the semiconductor and photovoltaic sectors. China dominates the market as the major producer and consumer in the Asia Pacific region, where a significant portion of the global market is located. Additionally, North America and Europe are crucial markets for high-purity quartz. The market for high-purity quartz is anticipated to grow over the upcoming years, propelled not solely by the semiconductor and photovoltaic sectors but also by emerging technologies such as 5G communications, artificial intelligence, and electric vehicles, which will intensify the demand for high-purity quartz.

The photovoltaic industry relies on the utilization of high-purity quartz in the manufacturing of silicon rods and cells. This is due to the requirement for low-temperature production processes and the need for quartz products with low impurity levels, excellent light transmission, and corrosion resistance^[31-33]. The global market demand for quartz products was estimated to be approximately USD 29.1 billion in 2022, with the semiconductor industry accounting for 65% of the consumption share. Between 2015 and 2022, the global market size for the semiconductor industry experienced an average annual growth rate of 7.98% [Table 2]. The global photovoltaic industry market was valued at USD 233.83 billion in 2022, as reported in the 2022-2023 China Photovoltaic Industry Development Research Annual Report. The current market share of quartz products is shown in Figure 3 below, which shows that the semiconductor industry accounts for more than half of the high-purity quartz industry. High-purity quartz finds applications in the semiconductor industry for 3C (computing, communications, and consumer electronics), ultra-clean wafer processing, and other related processes. Furthermore, various industries are witnessing a growing annual demand for high-purity quartz^[34]. Figure 4 shows the different types of quartz products available on the market.

MINERALOGICAL CHARACTERISTICS OF QUARTZ AND ITS IMPURITY FORMATION

Mineralogical characteristics of quartz

Quartz is chemically represented by the formula SiO₂, where the atomic composition consists of silicon and

Table 2. Global semiconductor industry market size from 2015 to 2022

Year	Market size/USD billion	Average increase
2015	3,352	7.98%
2016	3,389	
2017	4,122	
2018	4,688	
2019	4,123	
2020	4,404	
2021	5,559	
2022	5,735	

Data source: Huajing Industrial Research Institute, www.gaoxinzhaoshang.com.

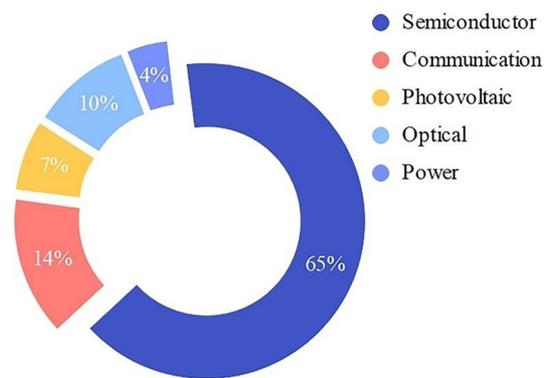


Figure 3. Consumption structure of quartz products in the market (Data source: China Mining Machinery Industry Market Foresight and Investment Planning Analysis Report).

oxygen atoms arranged in a three-dimensional pattern of ordered silicon and oxygen tetrahedra (SiO_4). SiO_2 has many homogeneous amorphous polymorphic variants and crystalline substances, and conventional quartz mostly refers to α -quartz, which is a quartz crystal composed of trigonal crystal systems that exist stably in an ordinary environment and is one of the homogeneous polymorphic variants of SiO_2 ^[35]. α -quartz can exist stably at 101.3 kPa and a temperature of 573 °C, and its stability increases as the temperature and pressure increase. α -quartz can withstand temperatures up to 1,380 °C and pressures up to 3.44 GPa^[36]. Figure 5^[23] shows the temperature and pressure conditions for various crystal forms of SiO_2 . In the Earth's crust, quartz is found in igneous, metamorphic, and sedimentary rocks, the main elements of which are shown in Figure 6^[35] below. Igneous rocks contain 93.6% of the total crustal quartz, while metamorphic and sedimentary rocks each account for 3.2%^[37].

Through thermogravimetric experiments, the researchers found that at 571.2 °C, α -quartz begins to transform into β -quartz. At 895.8 °C, β -quartz is converted to β -square quartz, but theoretically only at 870 °C^[38]. The formation of lepidote quartz begins at 1,199 °C. β -squared quartz begins at 1,338 °C, and at 1,500 °C, the alkali metal elements in quartz minerals play an active role in the conversion of quartz crystals to square quartz and the eventual formation of β -squared quartz at this temperature^[39-41]. β -phase quartz formation is important for the removal of iron impurities from quartz^[1,5,42]. Figure 7 shows the crystal structure transition diagram of quartz at different temperatures.

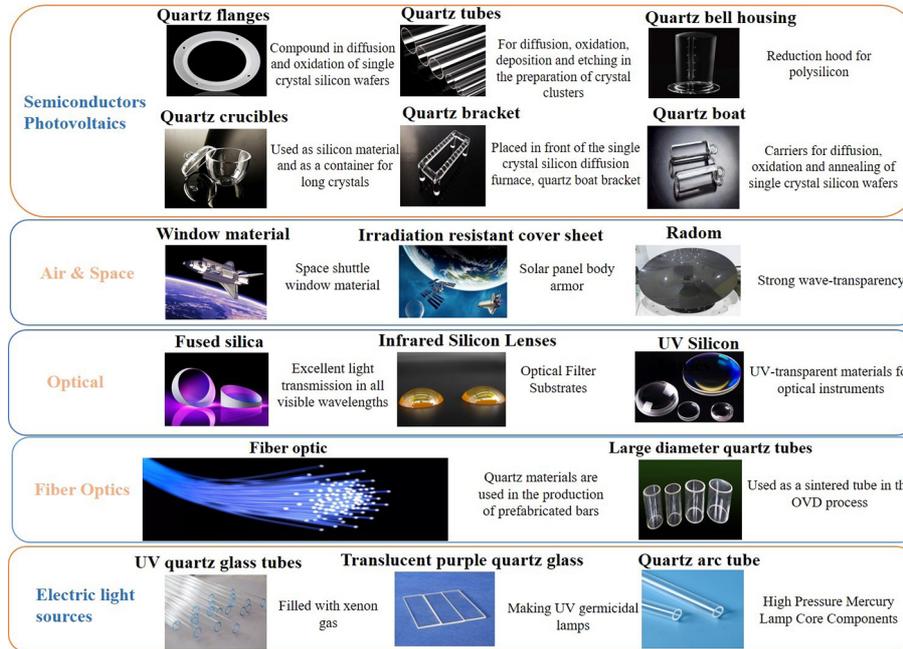


Figure 4. Various types of quartz products on the market.

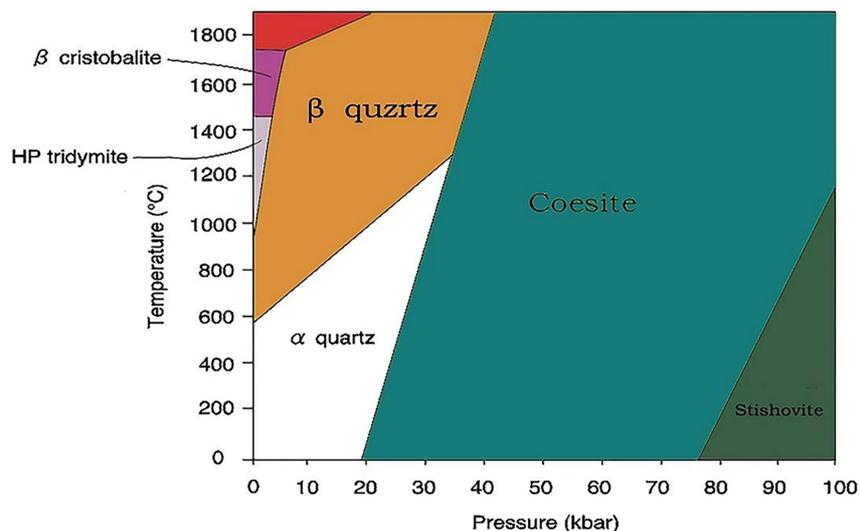


Figure 5. Temperature and pressure conditions for various crystal forms of SiO₂.

Analysis of impurity formation in quartz

In nature, the presence of 100% pure quartz is rare due to geological formations and various factors, leading to the inclusion of impurities such as Al, Fe, B, Li, Na, K, Ca, and other elements. The type of impurity present is influenced by the geological conditions during quartz formation. These impurities can be categorized based on their size, including lattice impurities, submicron inclusions ranging from 100 nm to 1 μm, nano inclusions smaller than 100 nm, and micro inclusions larger than 1 μm^[43]. For example, high-purity quartz in the market should contain less than 20 ppm of aluminum. However, aluminum impurities in quartz are present in the crystal lattice of quartz minerals in addition to being present in the form of compounds, and impurity aluminum in the crystal lattice is difficult to remove^[7,44,45].

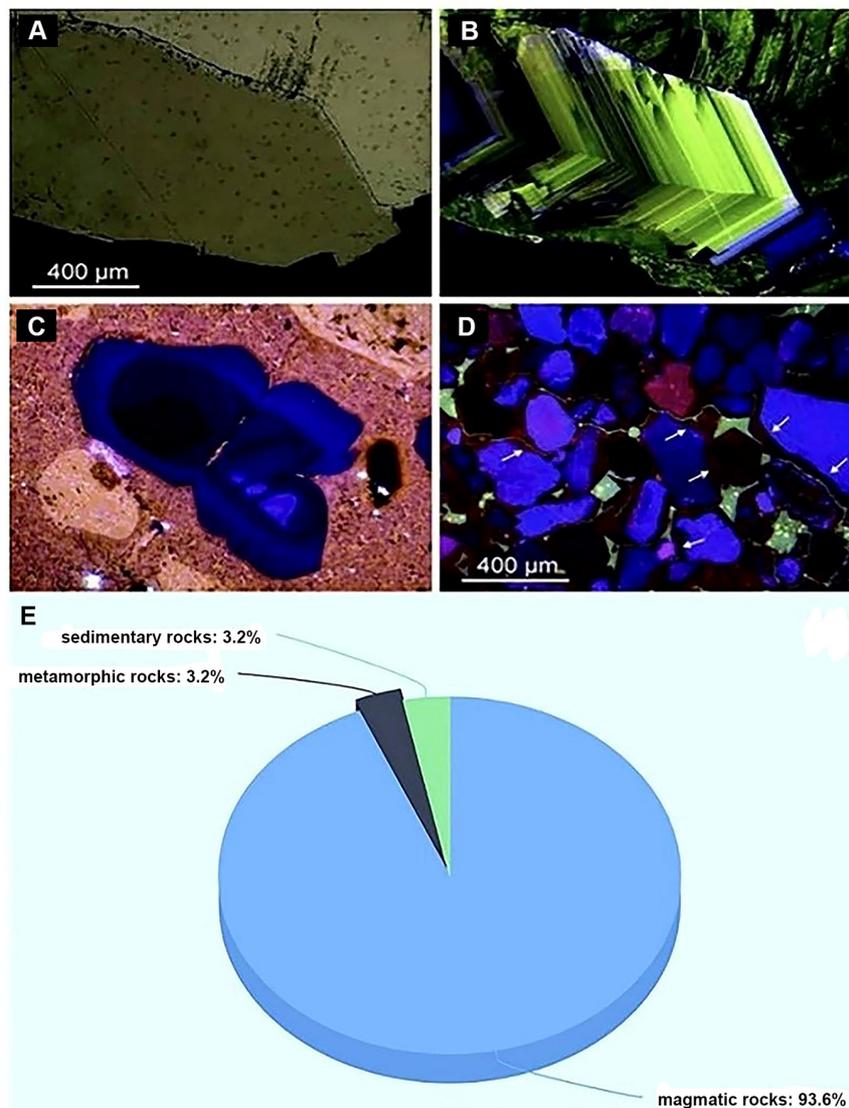


Figure 6. (A) and (B) Polarized light CL pairs of zonally grown crystals in hydrothermal quartz; (C) Photograph of CL quartz in rhyolite; (D) Photograph of CL quartz in sandstone; (E) Distribution of quartz content in the Earth's crust. CL: Cathodoluminescence.

In quartz crystals, there are three types of point defects: displacement atoms, gap atoms, and vacancies, and the presence of lattice impurities is closely associated with these defect types^[43]. The shapes of various impurities present in SiO₂ are illustrated in Figure 8A^[37,46]. The COHPs (crystal orbital Hamilton populations) of Si–O, Al–O, and Ge–O were calculated using MS software. All three bonds showed bonding states with negative COHPs. The bonding difficulty was found to be Si–O > Al–O > Ge–O in order [Figure 8B]. This indicates that the Al–O bond is more susceptible to breaking under external perturbations, making it favorable for the removal of lattice impurities. The substitution of Si⁴⁺ ions can be classified into two types. The first type involves unequal ion substitution, where the substituting ion possesses a different valence compared to Si⁴⁺. To compensate for the isomorphous ion substitution, additional charges are required, and compensating ions, such as K⁺ and Na⁺, migrate towards the atom's center, transforming into interstitial impurities in order to maintain electrical valence balance [Figure 8C]. The second type involves equivalent homogeneous substitution that does not necessitate charge compensating ions. Si⁴⁺ ions can be replaced by ions such as B³⁺, Fe³⁺, Al³⁺, Ti⁴⁺, Ge⁴⁺, and P⁵⁺ due to the negligible difference in radius between

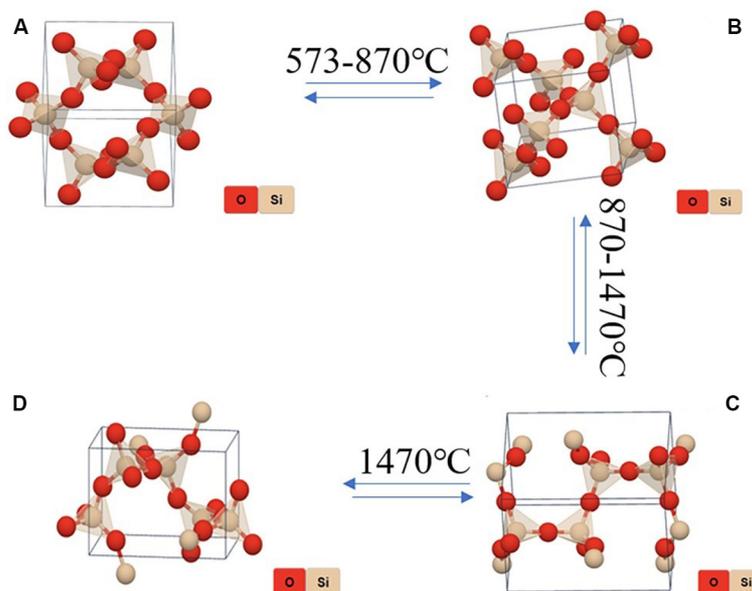


Figure 7. Diagram of the structural transformation of quartz crystals at different temperatures. (A) α-quartz; (B) β-quartz; (C) phosphor-quartz; (D) square quartz.

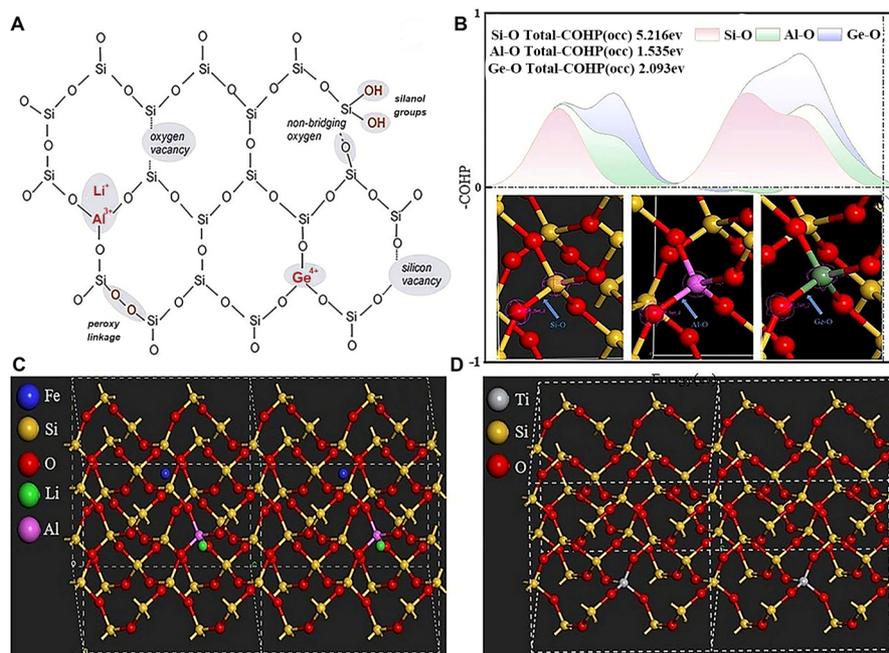


Figure 8. (A) Substitution of impurity elements in quartz crystals; (B) Bond energy calculations for Si-O, Al-O, and Ge-O; (C) Diagram showing the mechanism by which Al and Li atoms replace Si atoms; (D) Diagram showing the mechanism by which Ti replaces Si.

Si^{4+} and these ions [Figure 8D].

Müller *et al.* found that the purity of quartz was related to the elemental composition, replacement ions and interstitial impurity ions^[22]. The total number of moles of replacement ions B^{3+} , Al^{3+} , and Fe^{3+} is equal to the total number of moles of interstitial impurity ions K^+ , Na^+ , H^+ , Li^+ , and P^{5+} , where replacement ions and

interstitial impurity ions occur in pairs.

Submicron and nanoscale inclusions are predominantly observed in blue magma quartz^[47]. The occurrence of these inclusions can be attributed to three primary mechanisms. Firstly, they can arise simultaneously with the crystallization of quartz crystals. Secondly, they may result from the dissolution of previously crystalline minerals, forming solid solutions within the quartz structure. Lastly, the trapping of pre-existing crystalline minerals can contribute to the formation of nanoscale inclusions. Quartz crystals undergo concurrent crystallization with submicron inclusions, while nanoscale inclusions emerge as quartz crystals cool and dissolve in the form of solid solutions. Meng *et al.* learned from TEM analysis of samples that submicron and nanoscale inclusions are commonly found in quartz ores, while shapes occur in round or irregular shapes^[48]. Water molecular clusters less than 50 nm in diameter exist in fractures, subgrain boundaries, and dislocations in quartz, and these water molecular clusters exist in the form of bound water inside the quartz and as compensating charges in Si vacancies in the SiO₄ tetrahedron.

Microscopic inclusions observed in quartz crystals primarily comprise fluid and melt inclusions, readily observable under ordinary microscopes^[49]. Fluid inclusions, being the most abundant and prevalent, can be further categorized as primary or secondary, with their composition primarily consisting of H₂O, CO₂, and N₂, among others. Notably, fluid inclusions contain impurity elements such as K, Na, and Ca^[50]. On the other hand, melt inclusions consist mainly of silicate inclusions, usually found in igneous rocks, and impurity elements, including K, Na, and Li. Figure 9^[35,48,51] shows the various types of inclusions in quartz.

The lattice impurities in quartz are more difficult to remove than inclusions^[52]. The overall purity of quartz is influenced by the combined presence of these three material types. Physical purification methods such as magnetic separation, flotation, and calcination, along with conventional acid leaching techniques, are employed to eliminate microcrystals adhered to the quartz surface and certain microscopic inclusions. However, novel approaches must be explored to effectively remove lattice impurities, nano and sub-micron inclusions. This entails investigating the occurrence of lattice impurities, nano and sub-micron inclusions within the crystal lattice and comprehending their formation mechanisms. The fluid inclusions in quartz primarily consist of water, originating from bound hydrogen in the early quartz structure. Subsequently, through retrograde metamorphism, the water is formed and interacts with the surrounding rock to generate fluid inclusions^[53-55].

Most of the impurities in quartz are mixed in the quartz minerals in both bound and free form, except in the form of inclusions and lattice impurities. Figure 10A shows the XRD refined physical phase analysis of quartz minerals, which shows the three physical phase compositions in this type of quartz ore. Figure 10B shows SEM electron micrographs of quartz ores, which clearly show the distribution of impurities in quartz. Figure 10C shows a polarized light microscope photograph of this type of quartz ore, showing the shape and distribution of impurities. Figure 10D shows a polarized light microscope photograph of quartz ore after physical cleaning, and a comparison with Figure 10C shows that most of the impurity minerals have been removed.

Testing methods for quartz

Currently, the primary focus of silica sand analysis includes the determination of SiO₂ content, the detection of iron and aluminum levels, and the assessment of whiteness. High-purity quartz exhibits significantly high SiO₂ content, surpassing the capabilities of conventional chemical analysis methods and X-ray fluorescence (XRF). To identify trace impurities in high-purity quartz, various advanced techniques have been introduced, including ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry), GFAAS

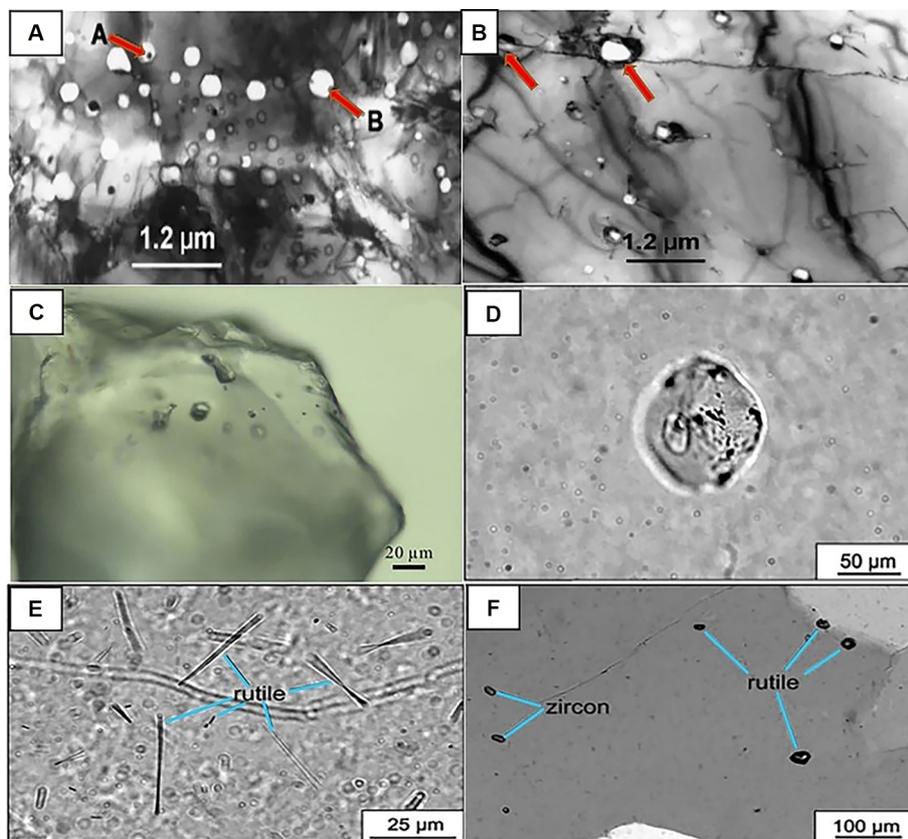


Figure 9. (A) Minor inclusions appearing at quartz dislocations, A and B are CO₂ in inclusions^[48]; (B) Fluid inclusions at grain boundaries; (C) Primary fluid inclusions with necking^[51]; (D) Silicate melt in quartz rutile^[35]; (E) Needles in quartz; (F) Rutile and zircon inclusions in quartz.

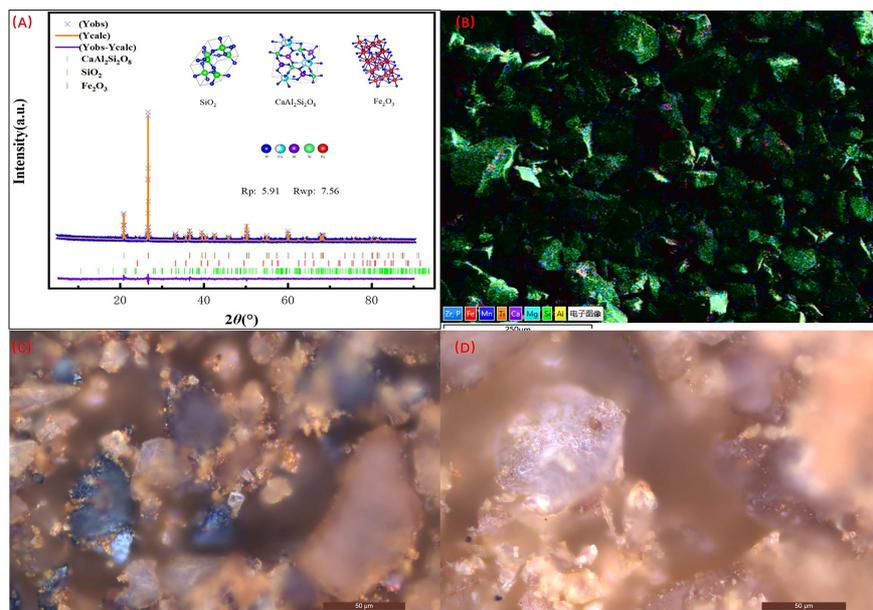


Figure 10. (A) XRD refined physical phase analysis of quartz mineral; (B) Shows an SEM electron micrograph of the quartz ore; (C) Photograph of this type of quartz ore under a polarizing microscope; (D) Polarized light microscope photograph of quartz ore after physical purification. SEM: Scanning electron microscopy; XRD: X-ray diffraction.

(graphite furnace atomic absorption spectrometry), FAAS (flame atomic absorption spectrometry), and TXRF (total reflection XRF)^[56].

The ICP-OES detection method relies primarily on exciting atoms or ions in the sample by using a high-temperature plasma, followed by measuring the spectral lines emitted by them at specific wavelengths to identify the presence and concentration of elements. This detection method is ideal for high-precision and multi-element analysis, as well as low detection limits and chemical complexity. The ICP-OES detection technique is characterized by utilizing high-temperature plasma for multi-channel analysis, enhancing the detection efficiency, incorporating calibration samples for accurate data collection, and performing quantitative and qualitative elemental analysis.

The principle behind GFAAS is a highly sensitive analytical technique used to analyze metallic elements. It involves drying and cauterizing samples dissolved in an acidic solution to atomize the metallic elements. The atoms are then processed with monochromatic light, causing them to emit light of different wavelengths. GFAAS is ideal for trace analysis, multi-element analysis, and the analysis of highly sensitive samples. The technology features automation and broad applicability but is limited to analyzing metal elements and high sample demands.

The main principle of operation of the TXRF technique is the use of an X-ray source to excite the electrons in the nuclei of the atoms in the sample. The jumping of the inner electrons produces XRF radiation, where each element has its own specific XRF spectral line. The main features of TXRF are high resolution, multi-element analysis, and high sensitivity. TXRF technology is often used in the fields of environmental, materials, and semiconductor sciences^[57,58].

Presently, quartz grades are categorized based on the impurity content in the quartz crystals. [Figure 11A](#)^[59] shows the criteria for quartz grading according to raw material price and mineral type. Quartz has cathodoluminescence properties, which can be used to analyze the composition of quartz and its microstructure^[60,61]. [Figure 11B-E](#)^[62] depicts different detection methods employed for analyzing quartz. The SEM-CL (Scanning Electron Microscopy-Cathodoluminescence) technique aids in obtaining a clearer visualization of the microstructural features of quartz, enabling researchers to gain insights into the spatial arrangement of impurities and their impact on the overall composition of the mineral. By employing SEM-CL, a comprehensive understanding of the impurity distribution within quartz can be obtained, facilitating subsequent purification processes.

Analysis of raw materials

Prior to commencing the purification of quartz, it is essential to conduct a thorough analysis of the raw material to determine its potential for attaining high purity. This analysis primarily entails examining the chemical composition of the raw material, including the presence of inclusions, lattice impurities, and co-occurring substances^[52]. Müller *et al.* have proposed and refined a criterion for identifying high-purity quartz, emphasizing the maximum permissible content of nine hazardous impurity elements within quartz [[Figure 11F](#)]^[43]. This criterion stipulates, for instance, that Fe should be below 3 µg/g, Al below 30 µg/g, and Na and K below 8 µg/g. The cumulative content of these nine hazardous impurity elements should not exceed 50 µg/g. In the presence of gas-liquid inclusions within the quartz mineral, these inclusions can be eliminated through high-temperature heating followed by rapid cooling using water quenching. Furthermore, lattice impurities can be removed via high-temperature chlorination roasting, while externally attached impurities can be eliminated through various physical and chemical methods^[63].

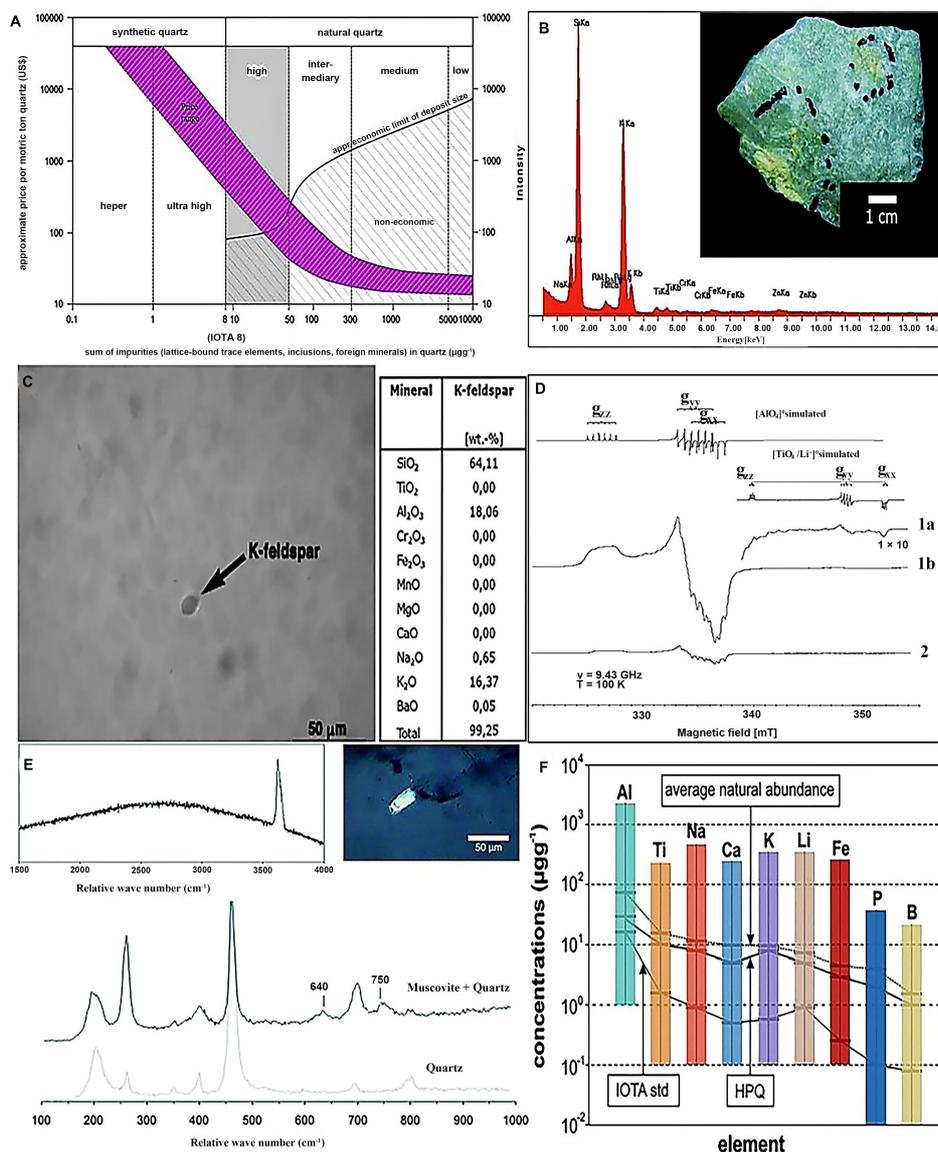


Figure 11. (A) Classification of quartz by raw material price and mineral type^[59]; (B) XRF analysis of potassium feldspar in quartz^[62]; (C) Electron probe microscopy of potassium feldspar; (D) EPR determination of elemental lattice impurities in quartz; (E) Raman spectroscopy of white mica inclusions in quartz Purification of quartz; (F) Upper limit of IOTA standard quartz and high-purity quartz element^[27]. EPR: Electron paramagnetic resonance; IOTA: International Oligomer Trading Association; XRF: X-ray fluorescence.

PURIFICATION METHODS

The raw quartz material undergoes preliminary and fine processing to attain the desired level of purity. Rough processing methods include water washing, scrubbing, flotation, magnetic separation, and ultrasonic treatment. These techniques aid in the removal of impurities and the enhancement of the quartz material's quality. Subsequently, the material undergoes finishing processes, such as high-temperature and high-pressure acid leaching, complexation using acids such as oxalic and acetic acid, high-temperature chlorination calcination, and microbial leaching. These advanced techniques further refine the quartz and contribute to the achievement of high-purity levels.

Physical pre-treatment

The primary objective of this stage is to reduce the raw material to a suitable size for cleaning, enabling effective separation of quartz crystals from associated minerals and facilitating the subsequent removal of fluid inclusions^[64,65]. Luo *et al.* used a wet ball milling process to ultrafine grind quartz minerals; the quartz particle size was measured after ball milling, and its particle size ranged from 0.5-3 μm , which was later analyzed by SEM and found to be passivated on the quartz surface^[66]. Mechanical crushing, high-pressure crushing, ultrasonic crushing, and current pulse crushing are the main methods used for crushing. The selection of the crushing method should consider its efficacy in separating quartz from associated minerals, avoidance of impurities introduction into the raw material, as well as its energy-saving and environmentally friendly characteristics.

Current pulse crushing

The current pulse crushing method has great advantages over other methods that use which use electric shock crushing and hydroelectric effect crushing^[67,68]. This crushing technique is primarily conducted in a water medium, where the application of high voltage current generates shockwaves that break the grain boundaries of quartz, selectively targeting inclusions. Notably, this method is gentle, preserving the essential morphological characteristics of the quartz raw material surface while remaining environmentally friendly, pollution-free, and energy-efficient. Figure 12^[68,69] illustrates the electrical resistance exhibited by various minerals, such as quartzite, in aqueous solutions, indicating their propensity to rupture at a voltage of 220 kV/cm within a time frame of less than 200 ns^[69]. Quartzite, being composed almost entirely of quartz with a uniform composition, displays minimal variations in dielectric constants among its crystal grains. During quartzite crystallization, there is a weak electric field distortion arising from crystallographic orientation, which is not easily dissipated. Conversely, sandstones exhibit significant differences in dielectric constants and compositions, rendering them more susceptible to fracturing. One notable advantage of pulsed discharge fracturing lies in its capacity to disintegrate impurity particles that accumulate among the silica oxides in water, thereby facilitating washing to remove a majority of surface impurities, primarily clay and iron oxides^[70].

Photoelectric sorting

Photoelectric sorting is a widely utilized method that employs the principles of photoelectricity to differentiate various impurity minerals. These impurity minerals in the color sorter will show different colors; external forces are then applied to change the trajectory of impurity minerals so as to achieve the purpose of separating impurities from the quartz sand. The main impurities in quartz sand are minerals such as potassium feldspar, mica, and sodium feldspar, which have similar physical properties and are difficult to remove by general methods. However, these minerals display certain differences in color and luster that can theoretically be used during color separation to enable their removal^[71]. For example, an increase in the concentration of elemental phosphorus or radiation causes a change in the color of quartz, and transparent quartz is selected from milky quartz, thereby reducing its alkali metal ion concentration^[72].

Rough processes

The main methods currently used for rough cleaning are washing, magnetic separation, flotation, and ultrasonic separation.

Ultrasonic scrubbing

The primary objective of the scrubbing process is the elimination of clay impurities, thin film iron, and unseparated mineral monomers adhering to the mineral surface. This removal is primarily accomplished through the application of mechanical force and friction between minerals. Subsequently, the minerals undergo classification and beneficiation to achieve further purification. Scrubbing can be divided into

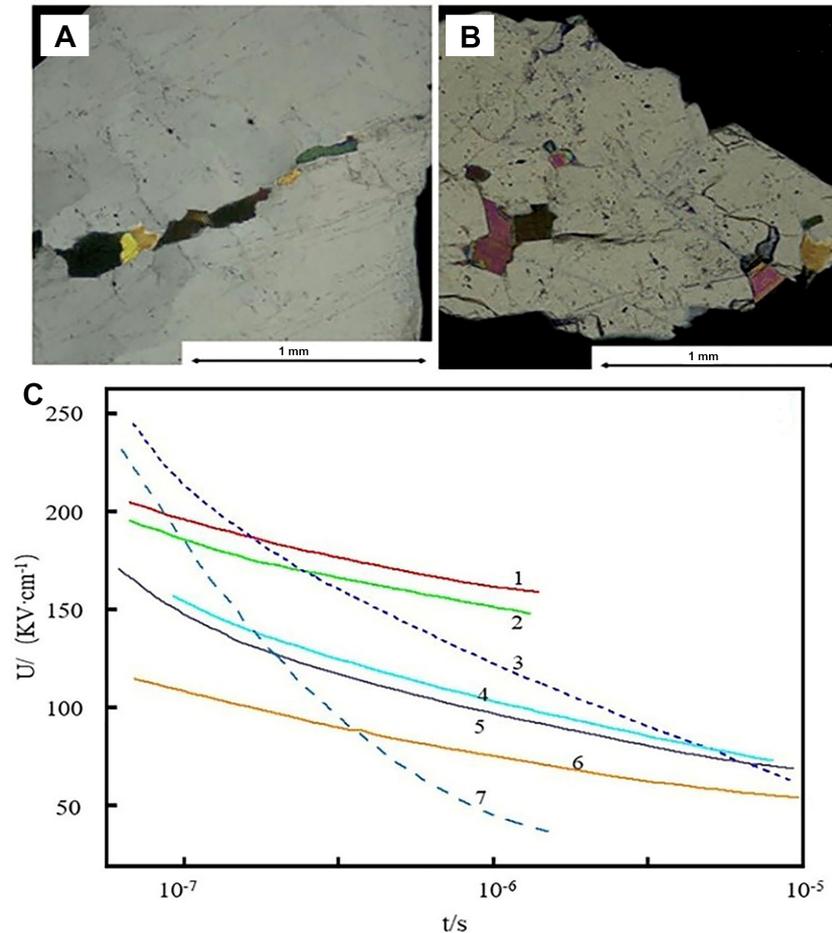


Figure 12. (A) Mechanically crushed quartz with few cracks and small black circles as mineral inclusions^[68]; (B) Quartz after current pulse crushing with many cracks and extensions around mineral inclusions; (C) Electrical resistance of different minerals: 1. Quartzite 2. Porphyry 3. Insulating oil 4. Dali Rock 5. Shale 6. Sandstone 7. Non-purified water^[69].

mechanical scrubbing and ultrasonic scrubbing. Mechanical scrubbing exhibits a recovery rate of merely 40%, which can be attributed to equipment-related issues, as well as the duration and concentration of the scrubbing process, both of which influence its effectiveness. Moreover, the principle of ultrasonic scrubbing is ultrasonic waves produced in the liquid to interact with quartz particles. This process results in the removal of the mineral surface impurity elements and hydration film. Further, by adding a dispersant to the liquid, these detachments will form a fine suspension, which achieves the purpose of purification after washing and cleaning^[73,74]. For example, Yang *et al.* found that the hydrophobicity of quartz particles increased significantly after ultrasonic treatment, resulting in a significant increase in quartz recovery from 64.66% to 77.54% after flotation^[75]. Additionally, Videla *et al.* showed that ultrasonic waves can improve the recovery of fine and ultrafine particles in mineral processing^[76].

Superconducting high-gradient magnetic separation

Superconducting High Gradient Magnetic Separation (HGMS) represents an advanced mineral processing technique employing superconducting magnets to establish a high-gradient magnetic field, thus facilitating the selective purification of valuable elements within ores. The superconducting magnets effectively generate a high-gradient magnetic field, enabling the segregation of impurity particles exhibiting varying magnetization coefficients within quartz ores. Specifically, magnetite is weakly magnetically selected, and

minerals such as garnet and ilmenite are strongly magnetically selected^[77]. The main advantages of the HGMS process over conventional magnetic separation are the continuous magnetic separation of the raw material stream, the high efficiency and recovery of the magnetic material, its clean and environmentally friendly production process, and its low cost. After magnetic separation is complete, scrubbing can be carried out again to further improve the purity and whiteness of the quartz^[78,79]. Moreover, the smaller particle sizes of the magnetic minerals lead to enhanced separation outcomes. For instance, Li *et al.* used HGMS technology to purify quartz from iron tailings with a SiO₂ content of 81.39% and obtained a quartz concentrate with a purity of 98.56%^[80]. The HGMS system, as depicted in [Figure 13](#)^[81-84], delineates the separation and purification process while also illustrating the particle size separation thresholds pertinent to this system.

Flotation process

The primary objective of quartz flotation is to eliminate associated minerals, primarily feldspar and micaceous components, while also achieving separation of iron and phosphorus-containing materials^[65]. This process differentiates hydrophilic and hydrophobic materials based on variances in their surface properties or modified surface characteristics. The main role of the flotation chemicals added during flotation is to act as capturing, foaming, and adjusting agents. In the flotation process, HF is added as an activator, H₂SO₄ is added as a stabilizer, and dodecylamine (DDA) ions are added as a scavenger. Quartz minerals possess a neutral pH in water and exhibit a negatively charged state. The primary role of DDA is to electrostatically bind to the hydrophilic amino groups present on the quartz surface, thereby maintaining distance from the hydrophobic carbon chain groups. This form of beneficiation is commonly referred to as fluorine beneficiation^[85,86]. Fluorine-free processing uses H₂SO₄ or HCl as an activator and is otherwise very similar to fluorine-based processing. Today's flotation processes use a mixture of scavengers, which are more effective and less costly than a single scavenger^[87]. For example, Chinese researchers used a mixed trap to purify silica sand by reverse flotation, and after rough and selective purification, the impurity removal rate was 53.96%, with Fe and Al removal rates reaching 84.15% and 37.50%, respectively^[87]. [Figure 14](#) illustrates the flotation process for both minerals, while [Table 3](#)^[64,88,89] presents the distinct means and characteristics of rough machining removal.

During the screening process for ores, it is recommended to utilize color separation for initial screening when the raw minerals display varying colors. For minerals with copious adherent films on their surface, scrubbing may be necessary for effective cleaning. Additionally, ores that display clear density differences, such as non-metallic ores (e.g., tungsten ore, tin ore, titanium ore) and metal ores (e.g., iron ore, lead-zinc ore, copper ore), can be easily segregated using common density separation techniques. Magnetic and non-magnetic minerals can be separated based on their varying magnetic susceptibilities. Meanwhile, flotation primarily relies on the interaction between particulate solids and air bubbles within water to isolate mineral particles with different adhesive properties. Consequently, this technique is frequently employed to recover metallic minerals such as copper, zinc, nickel, gold, and iron, as well as non-metallic minerals, including potash, phosphates, and gypsum.

Chemical pre-treatment

Plain calcined and high-temperature sulfide roasting

The thermal quartz crushing process reduces the hardness of the quartz and the energy required for crushing while also reducing the contamination caused by contact between the grinding media and the quartz. This process primarily involves subjecting quartz minerals to specific temperatures, inducing volume expansion and phase changes within the minerals. Consequently, gaps form on the quartz surface, facilitating subsequent cleaning steps aimed at eliminating impurities such as clay and iron oxides^[64]. High temperatures can destroy the structure of associated silicate minerals (feldspar and mica). Subsequent water

Table 3. Different rough machining techniques for separating impurities [64,88,89]

Sorting methods	Principle	The main impurities selected	Features
Color selection	Mineral optical properties	Dark impurity minerals, milky white quartz, etc.	Coarse-grained grades are highly effective
Scrubbing	Mineral particles rub against each other	Fine mud, oxide films, etc., adhering to the surface of quartz particles	Mechanical, dosing, ultrasonic scrubbing
Gravity beneficiation	Mineral density	Mica, zircon, rutile, etc.	High concentrate losses
Magnetic separation	Mineral magnetism	Magnetic minerals such as hematite, magnetite, tourmaline, and mica	Multi-stage strong magnetic separation
Flotation	Mineral surface properties	Mica, feldspar, apatite, etc.	Reverse flotation, multiple selection

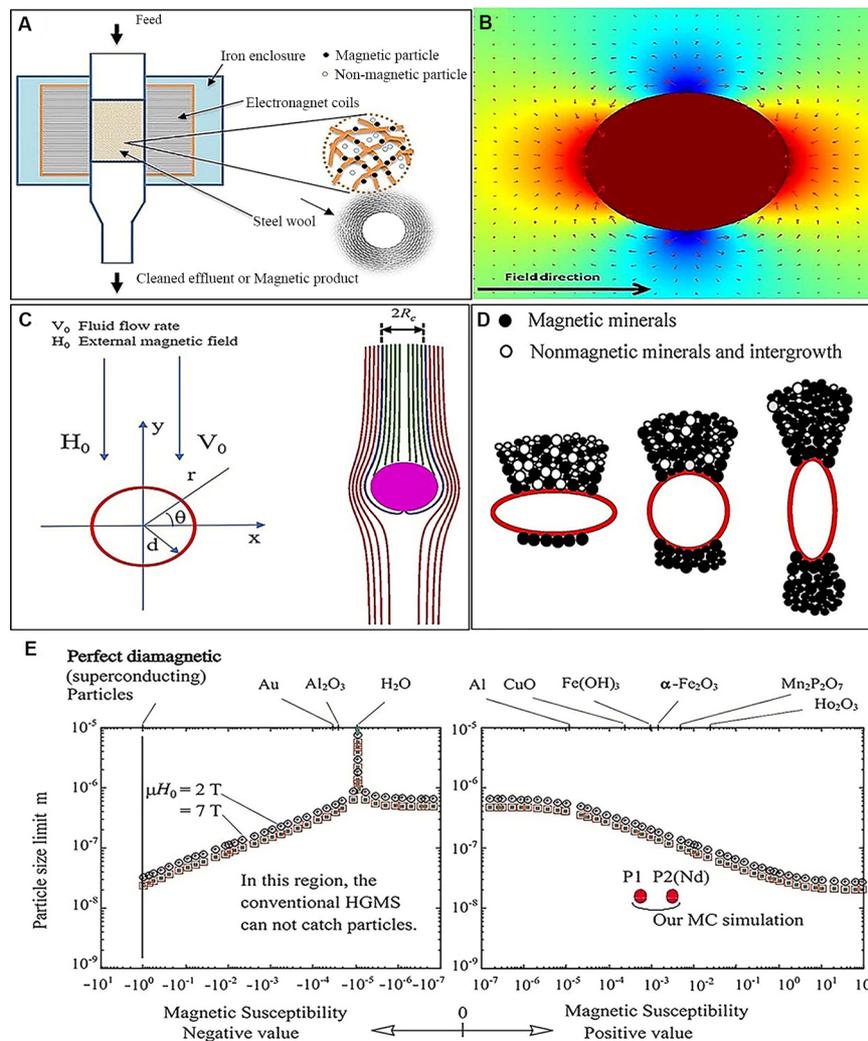


Figure 13. (A) Separation and cleaning flow of the HGMS system [81]; (B) FEM simulation of the magnetic field distribution near a circular cross-section substrate with the strongest magnetic field in the horizontal direction [82]; (C) Longitudinal distribution of particle motion trajectories near a circular cross-section, with escape trajectories in red, critical trajectories in blue, and capture trajectories in green; (D) Particle accumulation maps on different cross-sectional substrates [83]; (E) Particle size separation limits in the HGMS system, with circles ($\mu_0H = 2\text{ T}$) and boxes ($\mu_0H = 7\text{ T}$) as separation limit regions [84]. FEM: Finite element method; HGMS: High Gradient Magnetic Separation.

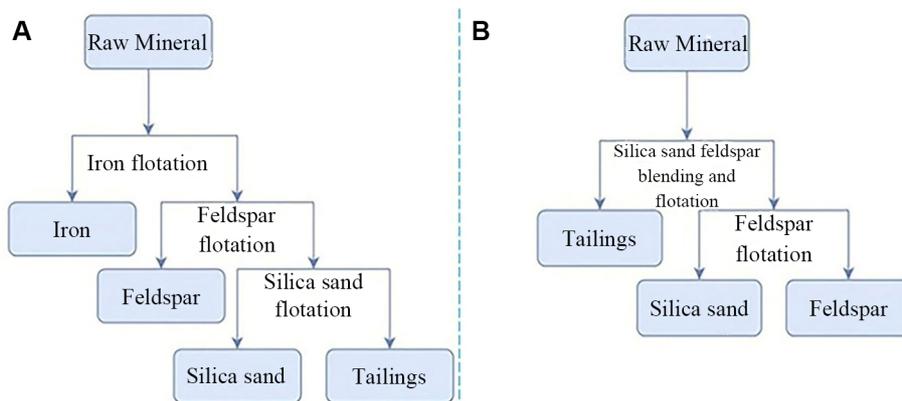


Figure 14. Two mineral flotation processes with a different order of separation of the components.

quenching following the roasting stage eliminates gas-liquid inclusions from the quartz. The calcination reaction equation is depicted in Equation (1)^[90,91].



During high-temperature calcination, the structure of impurity minerals (muscovite) within the quartz is destroyed, and new activated structures are formed due to the high-temperature environment. Figure 15A and B^[92] shows these activated structures (Al-O-K, Si-O-K, and Si-O-Al). The interaction of these activated structures with quartz produced new stable compounds capable of preventing K and Al from entering the quartz phase. At a temperature of 900 °C, the muscovite structure undergoes chaotic rearrangement of its atoms, accompanied by the evaporation of water. Consequently, the aluminum structure becomes deformed, thereby establishing the conditions conducive for subsequent pressure leaching aimed at removing muscovite. Zhang *et al.* studied calcination of quartz ore at a temperature of 900 °C for 4 h and found that the transformation of α -quartz to β -quartz reached 94.7%, and then combined with acid leaching for impurity removal; the removal rate was as high as 88.2%^[5]. The phase transformation and impurity diffusion of quartz crystals after high-temperature roasting are depicted in Figure 15C^[5].

For the further elimination of iron impurities from the quartz lattice, the addition of ammonium sulfate (AS) during the pre-treatment of quartz ore calcination can be employed. This is because the decomposition of AS generates sulfur dioxide (SO₂), with iron (III) oxide (Fe₂O₃) acting as a catalyst for the oxidation reaction of SO₂. Zhang *et al.* found that the reaction between SO₂ and Fe₂O₃ would convert trivalent iron ions to divalent iron ions, which exist as FeSO₄ and FeO, as shown in Equation (2)^[93]. Additionally, a model configuration illustrating the atomic-level reaction is presented in Figure 15D-F^[94]. When purifying quartz by adding AS, Du *et al.* found that acid leaching and color change analysis of samples roasted with the addition of AS at temperatures between 400-500 °C revealed that the redox-induced change in the valence of Fe during roasting played a dominant role in the removal effect of Fe impurities^[94]. The team also found that a decrease in Fe valence weakens the Fe-O bond between Fe and SiO₂, which is more favorable to the removal of Fe impurities.



High-temperature chlorination roasting

Conventional roughing makes it difficult to remove lattice impurities from quartz, and even when HF is

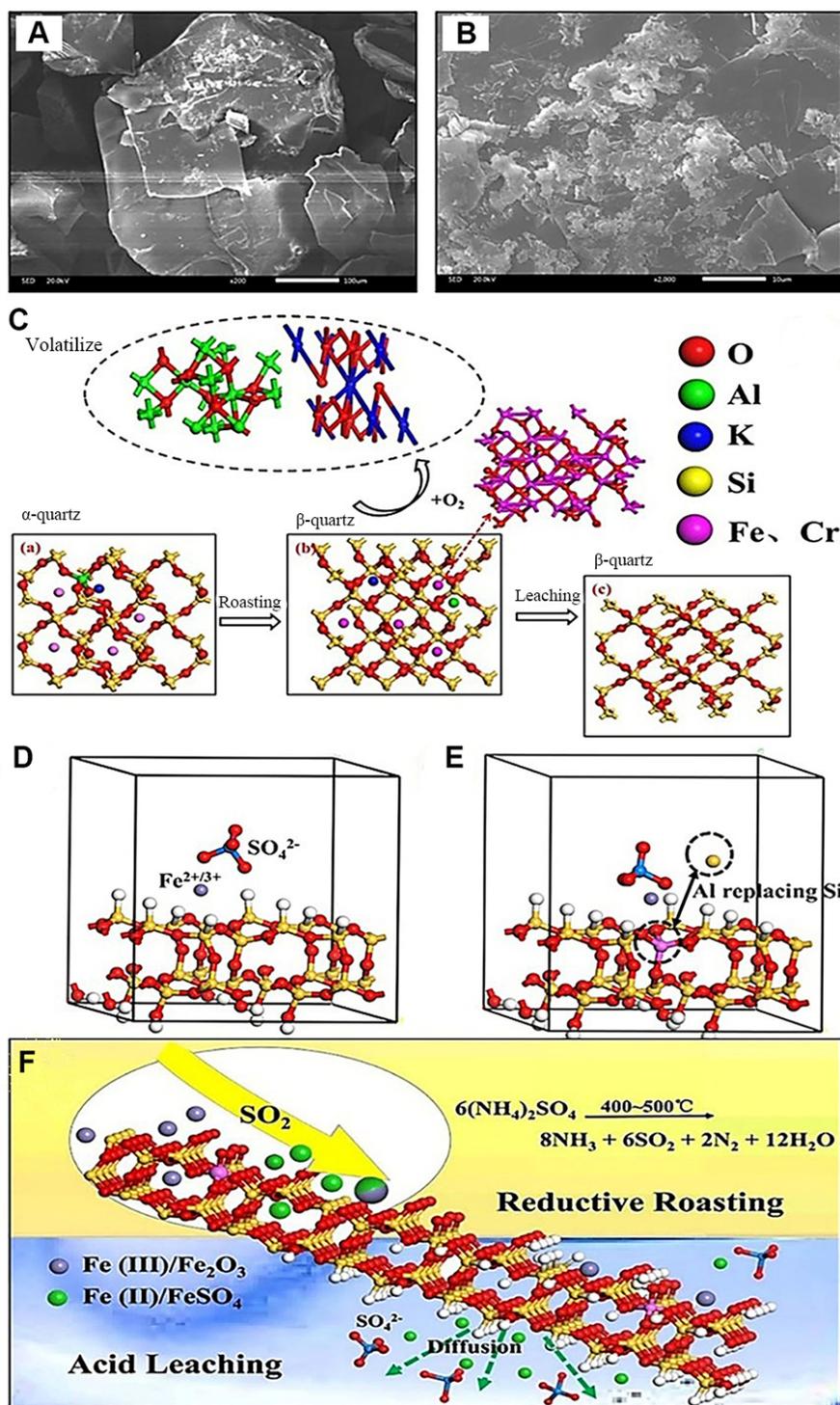


Figure 15. (A) disrupted muscovite structure; (B) fragments are micron-sized active structures; (C) Impurity diffusion diagram during high-temperature roasting and acid leaching^[5]; (D) Reaction configuration of impurity iron with sulfate ions in quartz crystals (101)^[94]; (E) Lattice substitution within quartz crystals to form impurity aluminum; (F) Atomic configuration of SO₂ reacting with trivalent iron.

introduced in the finishing process, it primarily targets impurities present at the surface^[95]. To address lattice impurities within the quartz, high-temperature chlorination and roasting pre-treatment can be used to remove the alkali metal elements within the lattice. During the reaction, the chlorinating agent reacts with

impurities in the quartz at high temperatures and forms chlorides, which, in turn, sublime and separate from the raw material to obtain high-purity quartz. The chlorinating agent can be Cl_2 , HCl , and NH_4Cl , although non-toxic substances such as NaCl and CaCl_2 are also commonly employed.

Yan *et al.* reduced the iron content from 66.4 to 0.8 $\mu\text{g/g}$ by high-temperature chlorination roasting combined with acid leaching^[96]. It is crucial to ensure that the introduced cations do not contaminate the mineral during the treatment process. For instance, due to their relatively large radius and limited diffusion within quartz crystals, potassium ions (K^+) are suitable for use as chlorinating agents, such as KCl . In a study conducted as early as 1980, Lin *et al.* discovered that K_2O possesses the ability to lower the phase transition temperature of α -quartz^[63]. During the process of calcination, KCl produces K_2O , which facilitates the migration of trace elements within the lattice to the quartz surface and subsequent accumulation during the phase transition of α -quartz. These accumulated impurities are later removed through acid leaching. Figure 16^[63] depicts the transformation from the α -quartz phase to the square quartz phase, achieved using the high-temperature chlorination calcination method at a d-spacing of 3.35. Moreover, hot pressure leaching effectively eliminates crystal defects resulting from lattice element deviations following high-temperature calcination, facilitating the separation of SiO_2 and lattice impurities.

Although high-temperature chlorination roasting is effective in removing Fe-like lattice impurities from quartz, it is less effective in removing Al^[97,98]. The level of Fe and Al impurities in quartz is an important measure of whether it can be classified as high-purity quartz. Impurity elements, such as Al, Ca, and Mg, possess a stronger affinity for oxygen compared to chlorine, thereby limiting the efficacy of chlorination roasting in removing Al impurities^[99]. Al is present in quartz ores in the form of clusters (clay, mica, and feldspar-like), inclusions, and lattice impurities. To address the removal of Al, a two-step approach can be employed. Firstly, high-temperature chlorination roasting and water quenching pre-treatment can be conducted, followed by hot press acid leaching. In this subsequent step, the leaching temperature and duration are increased to break the Al–O bond under high temperature and pressure conditions, thereby enabling Al removal.

Microwave roasting

Unlike traditional heat transfer methods, microwave heating involves the conversion of electromagnetic energy into heat by directly coupling with the material. This unique mechanism generates temperature gradients on both the material's surface and within its interior, resulting in reduced energy consumption and enhanced heating rates^[100-105]. The varying microwave absorption capacities of materials can be attributed to differences in their dielectric constants. Materials with higher dielectric constants exhibit greater susceptibility to microwave heating. For instance, while SiO_2 does not interact significantly with microwaves, Fe_2O_3 displays strong interactions^[106,107]. Therefore, inclusions containing Fe_2O_3 can be thermally cleaved and removed more easily. Li *et al.* used microwaves with selective heating characteristics to make tiny inclusions burst near the phase transition temperature, which produced cracks in α -quartz to β -quartz during the subsequent debinding process to reduce the diffusion of iron impurities^[108]. Then, acid leaching treatment with ultrasonic was used to reduce the iron content in quartz to below 0.167 ppm. Hou *et al.* concluded that microwave treatment can affect the fluid inclusions in quartz, accelerating the leaching of HF and the dissolution of silicates^[109].

The primary objectives of high-temperature roasting in the context of quartz purification are to eliminate water, remove organic impurities, and enhance the crystal structure. High-temperature sulfide roasting or high-temperature chlorination roasting is implemented to eliminate impurities present in the form of sulfides. There are differences in the reaction products of these two roasting methods, depending on the

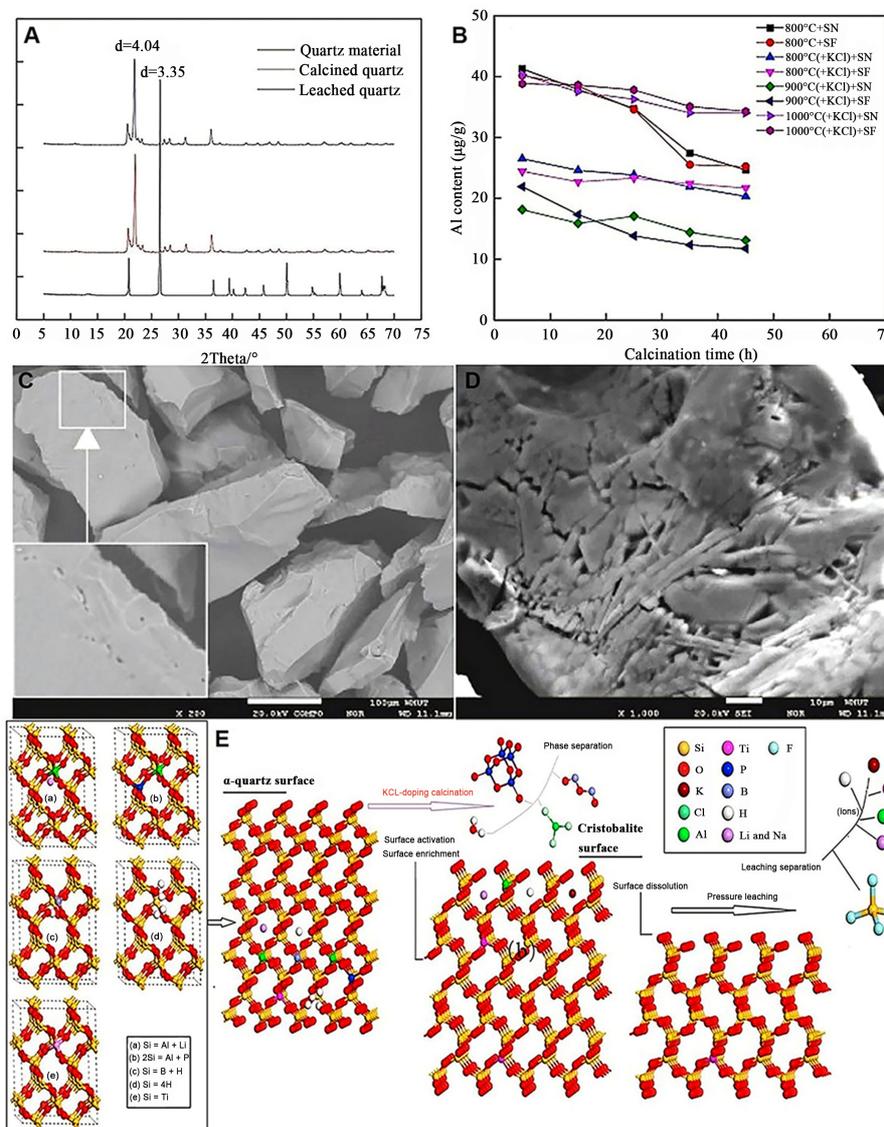


Figure 16. (A) XRD diagram after leaching and calcination; (B) Variation of Al content with roasting time under different leaching conditions (SN $H_2SO_4-NH_4Cl$ mixed solution, SF H_2SO_4-HF mixed solution); (C) Oxidative roasting of raw ore causing inclusions to burst and pits to form; (D) Cracking of quartz ore surface after roasting with KCl doping; (E) Diagram of precipitation of impurity ions during high-temperature chlorination roasting. XRD: X-ray diffraction.

compounds chosen for impurity removal. Chlorination roasting, in particular, has the potential to cause environmental pollution during the reaction process. On the other hand, microwave roasting is distinct from traditional roasting methods, as it can achieve uniform heating and is more energy-efficient than the above-mentioned methods.

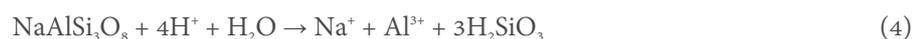
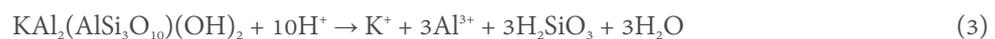
Finishing processes

High-temperature acid leaching

After rough processing of the quartz raw material, most of the surface adherent impurities and some mineral inclusions have been removed. Nevertheless, meticulous microscopic examination reveals the persistent presence of iron-like substances and minute mineral inclusions on the concentrate's surface. Acid leaching, employing substances such as HCl, H_2SO_4 , HF, citric acid, and oxalic acid, can effectively eliminate these contaminants^[110]. The purification of SiO_2 by acid leaching falls within the field of hydrometallurgy,

but there has been little research into the purification of non-metallic minerals using hydrometallurgical techniques^[111,112]. As shown in [Figure 17](#)^[94], a large amount of Fe₂O₃ impurities from the surface of quartz are removed after physical cleaning, and some fine impurities remain within the lattice interstices.

The principle of acid leaching is mainly to use the H⁺ provided by the acid to dissolve the feldspar-like and mica-like minerals in quartz with the reaction Equations (3) and (4). However, in the absence of any catalytic assistance, the reaction proceeds at an exceedingly slow pace^[113,114]. To achieve the desired leaching effect, mixed acid leaching with high temperature, high pressure, high temperature, and catalytic hot pressure techniques are often used. HF has an excellent leaching effect, and its leaching mechanism is to break the Si–O and Al–O bonds between aluminosilicates; however, the use of HF can pollute the environment^[115]. Consequently, the cleaning process should be tailored to the properties of the mineral, and the use of HF should be minimized. When acids are employed, acid consumption should be reduced to make the cleaning process highly efficient, environmentally friendly, and cost-effective.



High-temperature leaching is a technique that involves heating an agitated water or air bath in a semi-enclosed environment [[Figure 18](#)]^[23]. The method employs acids to separate quartz minerals from silicate mineral impurities and partly removes impurities within the lattice structure. The challenge of leaching impurities varies as follows: quartz > potassium feldspar > sodium feldspar > white mica. Furthermore, high-quality quartz is purified more effectively than low-quality quartz. Nonetheless, leaching remains slow despite the utilization of external heating to speed up the purification process. To enhance the reaction speed and decrease acid usage, the raw material can be pre-treated before leaching.

Tuncuk^[116] achieved 98.9% Fe₂O₃ removal after the addition of H₂SO₄ and H₂O₂ using oxalic acid as the reducing agent. Zhang *et al.* made the purified quartz concentrate between 3 and 4 N by magnetically separating the quartz ore, followed by acid leaching in combination with H₂SO₄ and HCl^[117]. Zhou treated feldspar, mica, and crystal separately with mixed acids at room temperature and found that the feldspar-like substances were more soluble than the other two^[112]. This method boasts wide applicability, but acid consumption and contamination pose significant challenges that impede its further development.

High-temperature and high-pressure leaching

A hot pressure acid leach system is a reaction system employed in wet metallurgy made of stainless steel and p-hydroxylated polystyrene, although other alternative materials can be used. It is equipped with both an internal and an external double seal to ensure efficient operation. [Figure 19](#)^[92] illustrates the high-temperature and high-pressure leaching system, showcasing the variations in impurities such as Al and K throughout the leaching process. The inner layer of the system contains the leach and the treated minerals, with a choice between single acid or mixed acid as the leach. The temperature is carefully regulated at approximately 170 °C, while the L/S ratio is maintained between 4-8 L/kg^[118,119]. The primary objective of this method is to remove mineral inclusions and symbionts. The hot press environment disrupts the structure of the silicate minerals and facilitates the entry of acid into the fractures and the reaction of the alkali metal elements, thus completing the delimiting process. Zang *et al.* achieved an impressive purity of 99.994% for SiO₂ utilizing hot pressing leaching^[120]. This process induces distortion in the quartz lattice, enhancing the leaching of impurities residing in the lattice interstices. The ease with which individual impurity minerals are leached from quartz is consistent with high-temperature leaching. Xiong *et al.*

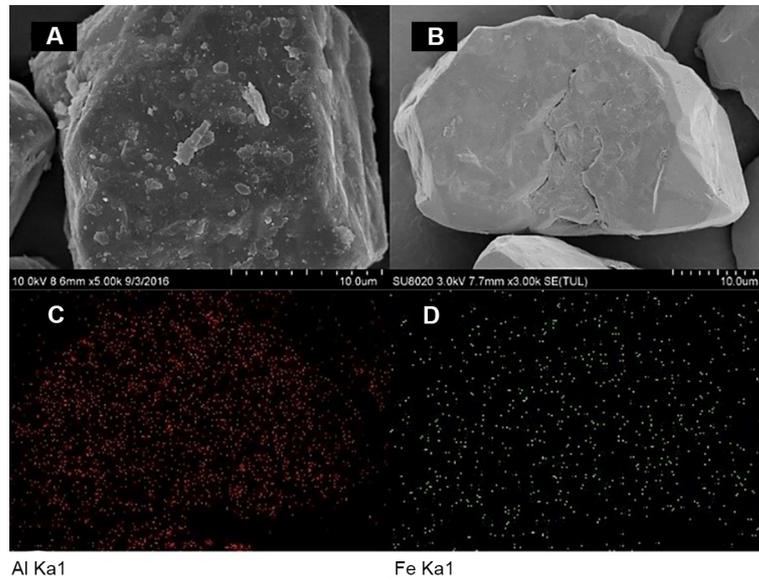


Figure 17. (A) and (B) SEM images of quartz minerals before and after physical purification, respectively; (C) and (D) EDS images of residual impurities. EDS: Energy dispersive spectrometer; SEM: scanning electron microscopy.

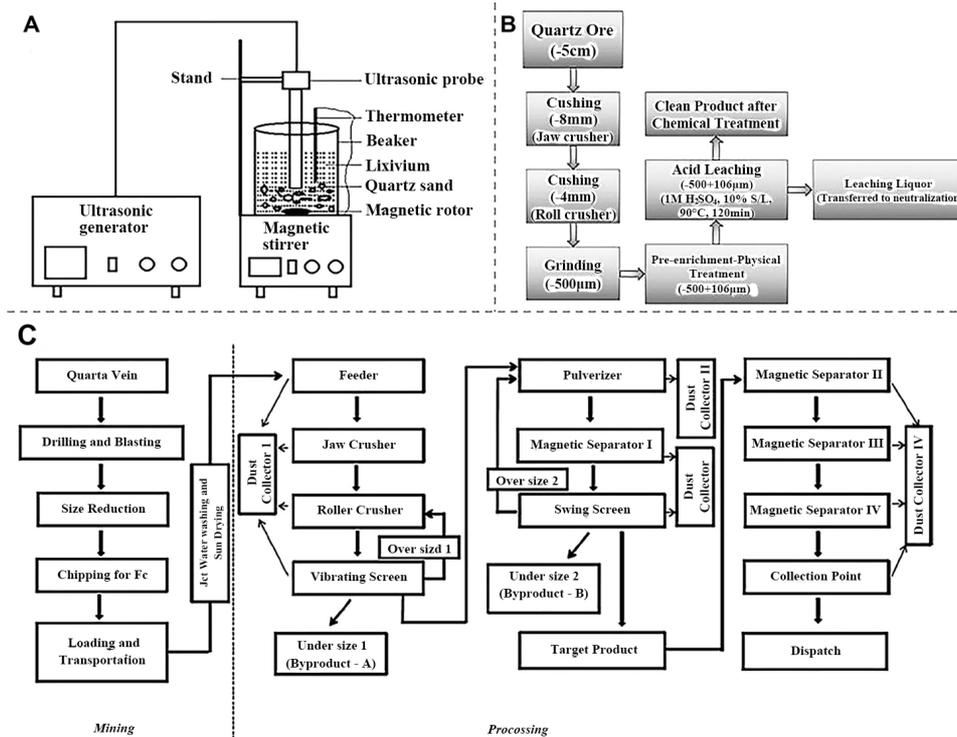


Figure 18. Semi-closed high-temperature leaching system.

achieved a SiO_2 content of 99.996% and a total impurity removal of 86.96% in the treated quartz using hot-press acid leaching^[121].

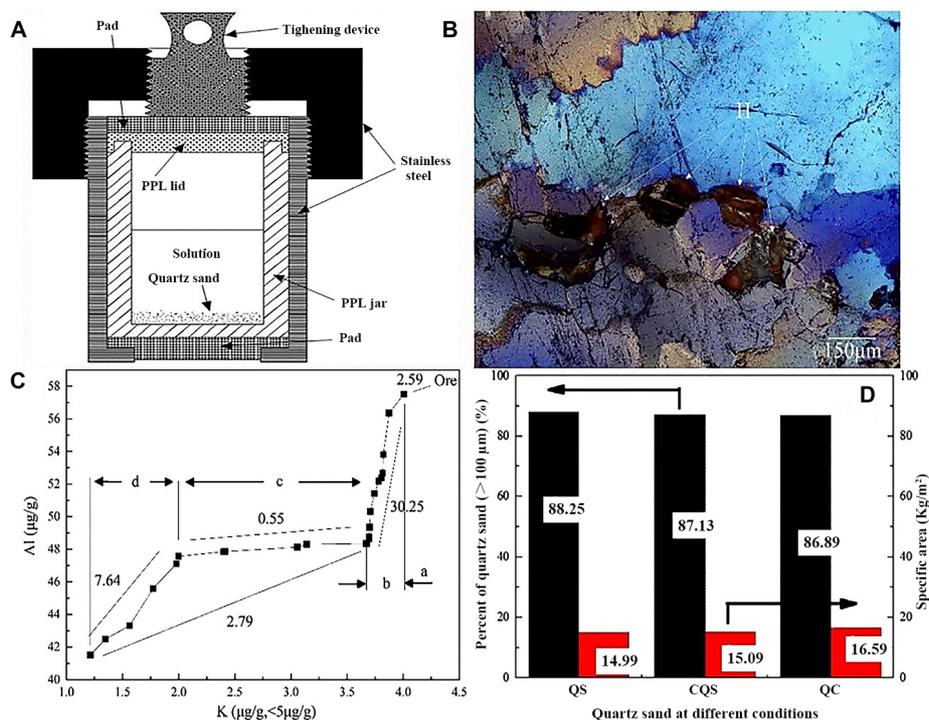


Figure 19. (A) High-temperature and high-pressure leaching system; (B) leaching of the treated hematite ore; (C) variation of Al and K during leaching; (D) variation of the leaching efficiency of the vein minerals from different quartz feeds. CQS: Calcined quartz sand; QC: quartz concentrate; QS: quartz sand.

Catalytic high-temperature and high-pressure leaching

In the present era, as environmental protection has gained significant global attention, researchers have explored more eco-friendly alternatives to high-temperature leaching and high-temperature and high-pressure leaching methods. Consequently, a catalytic high-temperature and high-pressure leaching approach has been proposed^[122]. The reaction apparatus employed in this method bears resemblance to the hot press apparatus. The leaching environment is maintained at approximately 265 °C, and the chemicals utilized include $\text{H}_2\text{SO}_4\text{-NH}_4\text{Cl}$ and $\text{HCl-NH}_4\text{Cl}$ components. Notably, NH_4Cl serves as a catalyst, facilitating the dissolution of Fe_2O_3 and the removal of micaceous impurities. Since the Al–O bonds in the reaction are more easily broken than the Si–O bonds, the temperature and the Si–O bonds in the reaction promote a hydrolysis reaction of Al^{3+} , which results in the binding of Al^{3+} and Si–O bond structures to each other, as shown in Equations (5) and (6). In this environment, NH_4Cl undergoes a hydrolysis reaction to produce additional H^+ , while NH_4^+ does not participate in the leaching reaction, thus providing a more stable environment, as shown in Equations (7) and (8).



This technique is ideal for quartz ores with a SiO₂ concentration of 3 N or higher, as it omits the requirement of fluorinated raw materials during the process. Furthermore, it uses merely 10%-30% of the acidic consumption associated with the previous two approaches. By implementing this approach, the ultimate purity of SiO₂ can reach 4-5 N, and the reaction duration is significantly reduced. However, this approach is pricier than the two aforementioned methods and requires optimization. Figure 20 shows the process flow diagram of normal acid leaching and high-temperature and high-pressure leaching.

Microbial leaching

Although leaching can effectively purify quartz minerals and yield high-purity quartz, it is accompanied by a significant drawback of generating a substantial volume of waste acid, thereby posing adverse environmental implications. Consequently, microbial leaching emerges as a promising alternative for quartz mineral purification, offering a green process that ensures true zero pollution. In the context of microbial beneficiation, when the targeted minerals lack the necessary nutrients for microorganisms, heterotrophic bacteria and fungi can be employed to treat them, providing an organic carbon source that serves as a nutrient for the microorganisms. Microbial beneficiation is a low-cost, environmentally friendly purification method that uses the metabolic material of microorganisms to react with the silicates in the mineral to remove impurities. Furthermore, the biological activity of fungi hinges on the production of organic acids, including oxalic and citric acid. Notably, the citric acid derived from the metabolic processes of *Aspergillus niger* triggers a complexation reaction with iron impurities, leading to their removal. This is because silicate bacteria metabolize organic acids such as oxalic, citric, and malic acids by absorbing K⁺ from silicate minerals, which contain substantial amounts of H⁺. Consequently, these H⁺ ions react with impurity minerals present in the ore, such as mica and feldspar, resulting in their elimination^[123,124]. Figure 21 illustrates the process of microbial reaction with minerals.

In a study conducted by Arslan *et al.*, strains of *Aspergillus niger* and *Aspergillus ficuum* were employed to address iron impurities in feldspar, demonstrating removal efficiencies of 70.13% and 85.09%, respectively^[16]. Despite the environmental friendliness and cost-effectiveness of this method, it still faces challenges in terms of industrial implementation due to prolonged leaching times, technological immaturity, and the complex nature of minerals.

CONCLUSIONS AND PROSPECTS

The initial stage in upgrading low-grade quartz minerals to high-purity quartz involves a physical pre-treatment aimed at eradicating surface impurities and disintegrating quartz grain boundaries to reveal inclusions for later elimination. Subsequently, superconducting HGMS and other coarse cleaning techniques are employed in the second stage to eliminate magnetic impurities (mainly iron) and silicate impurities from the quartz minerals. The third stage involves chemical pre-treatment, specifically high-temperature chlorination roasting. In the final stage, organic acids are used for catalytic high-temperature and high-pressure leaching, or microbial treatment is utilized to further reduce the levels of iron and aluminum present in quartz. It is worth noting that the entire process is free from HF, resulting in an eco-friendly, high-purity silica sand of 4-5 N purity. Furthermore, the procedure promotes the secondary use of high-silica mineral resources. These results are instrumental in propelling the quartz sector towards heightened energy efficiency, operational effectiveness, and environmental sustainability. Simultaneously, as the refinement method is being optimized, the possibility of combining industry, academia, and research is being explored to convert waste into valuable assets.

Given the global depletion of crystal concentrates, researchers across the planet are actively exploring the extraction of high-purity quartz sand from high silica tailings, with the objective of promoting resource

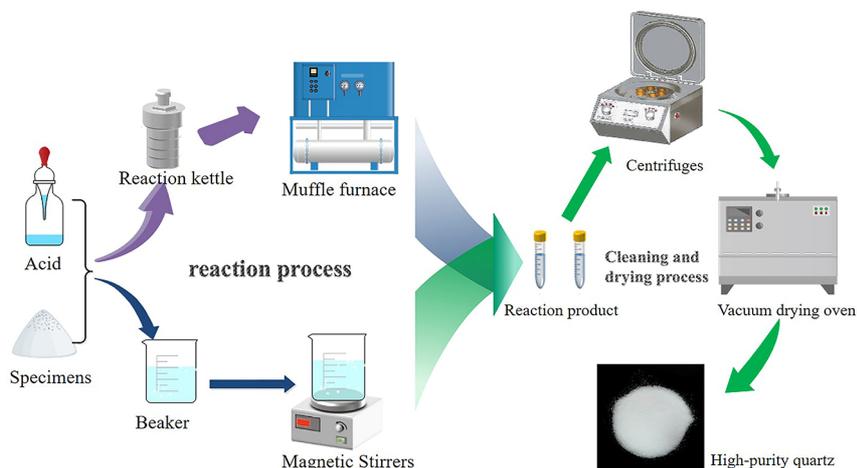


Figure 20. Flow chart of quartz conventional leaching and high-temperature and high-pressure leaching.

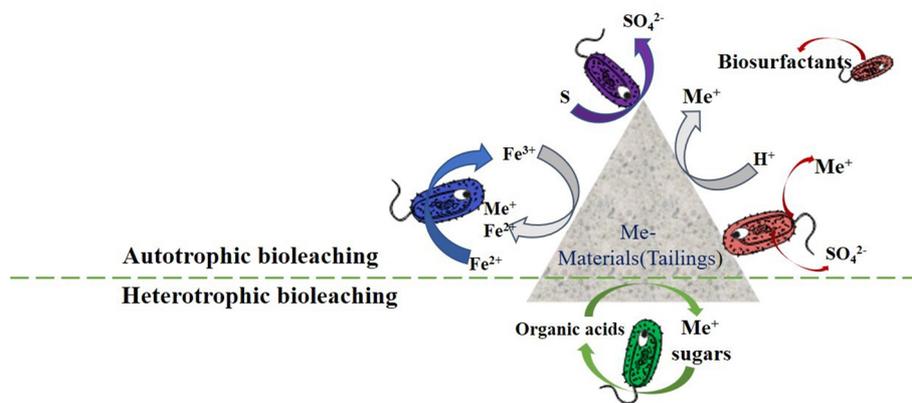


Figure 21. Illustration of the mechanism of leaching of valuable elements by various microorganisms.

reuse and cost reduction in high-purity quartz production. Present purification research primarily focuses on the technical aspects, yet there is a lack of comprehensive investigations into the theoretical study of impurity element transformation and migration patterns within quartz facilitated by different leaching agents, as well as the mechanisms underlying the removal of various types of inclusions in quartz. The utilization of highly polluting agents such as HF and nitric acid as leaching agents for purification poses significant environmental risks. In this regard, the adoption of organic acids such as oxalic acid and citric acid is recommended to attain maximum purity and environmentally sustainable production. To achieve truly acid-free and eco-friendly leaching, microbial leaching should be further developed for future high-purity quartz purification processes. Additionally, gas phase purification technologies employing raw materials such as SiCl_4 are being explored to achieve low-cost, high-yield, and environmentally conscious outcomes in SiO_2 purification.

DECLARATIONS

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Author' contributions

Material preparation and data collection and analysis: Xie Y, Pan X, Li Y, Zhang A

Written the first draft of the manuscript: Xie Y

Commented on previous versions of the manuscript: Li S, Pan X, Li Y, Zhang A

Communication, revision, and editing of the review: Li S

All authors contributed to the conception and design of this study. All authors read and approved the final manuscript.

Availability of data and materials

The data and materials presented in this article are available upon request.

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Conflict of interest

All authors declared that there are no conflicts of interest.

Ethics approval and consent to participate

Not Applicable.

Consent for publication

Not Applicable.

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