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**ADVANCED MINERALOGICAL ANALYSIS OF QUARTZ-
RICH SANDS USED FOR THE INDUSTRIAL PRODUCTION
OF GLASS**

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ABSTRACT

Glass is a versatile and technologically significant material with widespread applications, making it a critical component of modern industrial economies. Its production relies primarily on silica (SiO_2), which serves as the fundamental structural constituent and is typically sourced from natural deposits such as silica sand or quartz pebbles. The quality of these raw materials is of paramount importance, as the presence of impurities can adversely affect the physical, optical, and chemical properties of the final glass products. This study aims to quantify and characterize accessories minerals and contaminants present in silica-based raw materials used in glass manufacturing. A comprehensive set of analytical techniques was employed to evaluate the nature and concentration of impurities, both in the raw materials and in the resulting glass products. Particular emphasis was placed on the mineralogical composition of quartz-rich sands, with a focus on identifying light and heavy minerals and assessing the levels of iron (Fe) and titanium (Ti), which are known to significantly affect the glass quality. The results reveal the presence of various impurity-bearing minerals, including zircon, kyanite, andalusite, tourmaline, epidote, muscovite, rutile, and hematite. These minerals contribute to undesirable coloration and defects in glass, thereby limiting its industrial applicability. Therefore, accurate and efficient identification of such impurities is essential for improving raw material selection and ensuring compliance with product quality standards. Impurities detected in final glass products may originate either from the raw materials or from contamination introduced during various stages of the industrial manufacturing process, including interactions with furnace refractory linings. However, the identification of such inclusions using conventional optical microscopy remains challenging due to their encapsulation within the glass matrix, their variable optical properties, and their often-ambiguous morphology. These limitations make it difficult to reliably determine the origin and nature of the impurities. To address these challenges, this study explores the application of Raman spectroscopy as a rapid and non-destructive analytical technique for the direct identification of mineral inclusions within glass. Due to the inherently low Raman scattering of the glass matrix, spectra from embedded impurities can be effectively acquired by focusing directly on the inclusions using an appropriate excitation source. The performance of this method was evaluated through comparison with conventional optical identification carried out by experienced quality control operators. The comparison highlights the limitations of traditional approaches, which rely

primarily on visual assessment (e.g., shape and colour) and operator expertise, rather than on definitive chemical and crystallographic information.

In addition, granulometric analysis was performed on selected raw material samples to evaluate particle size distribution and to identify the grain-size fractions with the highest purity. Grain fractionation enabled the assessment of impurity distribution across different size classes, providing further insight into the suitability of the raw material for industrial applications. The results indicate that the analysed sand deposits, while not sufficiently pure for high-quality colourless glass production, are suitable for the manufacture of coloured glass.

Therefore, this work provides a comprehensive Raman spectral database of the most common impurities encountered in the glass industry, offering a standardized reference for application across different production plants. The proposed methodology enables accurate, in situ, and real-time identification of contaminants, significantly enhancing the ability of operators to detect and distinguish impurities with greater accuracy and efficiency. Ultimately, this approach facilitates improved traceability of contamination sources within the production cycle and supports higher quality control standards in glass manufacturing.

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1. INTRODUCTION

1.1 Overview

Glass stands as one of the best recyclable amorphous solid and environment friendly materials available in this era, due to its exclusive sustainable properties. Glass is believed 100% recyclable and can be recycled infinitely without losing its quality or purity. This infinite recyclability makes it a cornerstone material in the circular economy. This means that glass products can be collected, reprocessed, and remanufactured repeatedly, contributing to reduced landfill waste and conservation of resources. The sustainability of glass extends beyond its recyclability as glass is a chemically stable and non-toxic material. It does not leach harmful substances into food, liquids, or the environment, making it a safe choice for packaging, storage, and construction. This inertness not only protects human health but also reduces the risk of environmental contamination, supporting cleaner production and usage cycles. Therefore, it is understood that glass is an essential material in our daily lives, used in a comprehensive range of products that we depend on. Its manufacturing is a process that involves the production of glassware, playing a key role in sectors from basic utensils to essential products used across a range of global industries, from retail to transport as well as home and leisure. Worldwide, the container glass sector is the world's largest glass sector, which includes products utilized in packaging foods, beverages, cosmetics, pharmaceuticals, etc (Testa et al., 2017). With this, glass continues to be a versatile material that has numerous applications for a variety of businesses, making glass manufacturing an important part of the economy.

Glass manufacturing is a high-volume process, during which large quantities of substances and raw materials are turned into commercial products, consuming large amounts of non-renewable resources and energy in the process. Nowadays, there are four major sectors in the glass industry across the world i.e. container glass, flat glass, fibre glass, glass for specialist users (optical, lighting, laboratory). The primary raw material used for glass production is naturally occurring silica sand which is characterized by having high content of quartz (approx. 95% - 99% SiO_2) (Wang et al., 2025). Depending on the type of glass product, various other raw material is also added along with quartz rich silica sand to achieve the desired properties and characteristics of the final glass products. Most of the commercial glasses in everyday use, such as bottles and jars (containers), and flat glass (windows, mirrors and vehicle glazing), are soda-

lime-silica glasses. Mainly, for glass manufacturing, 60–75% silica sand or glass cullet is fused with a flux, typically soda ash (Na_2O) and lime, at temperatures of 1450 °C or higher (GWP Consultants LLP, 2010), as materials are incorporated depending on the desired properties of the final glass product. Therefore, nowadays, particularly, in glass manufacturing, cullet (crushed glass ready to be recycled) is also employed as a batch material, substituting for virgin raw materials (Roudier et al., 2013). Cullet is classified as internal or external if it derives, respectively, from imperfect products rejected at quality control during the industrial process of glass manufacturing and production cut-offs or from waste glass collected and/or reprocessed for recycling.

Principally, it is now obvious from the above discussion that the high purity quartz has been a vital raw material for production of good quality glass. The value of silica sand is influenced by several factors, including its level of metallic impurities, and its narrow grain size distribution e.g., 0.1–0.5 mm (Burkowicz et al., 2020; GWP Consultants LLP, 2010). Therefore, silica sand must be pure, comprising very low levels of metallic impurities such as Al, Fe and Ti, which can severely compromise the quality of the silica glass. Quartz for silica glass production must also contain low amounts of fluid inclusions. Such inclusions can produce bubbles during the fusion of the raw material into silica glass (Griscom, D.L., 2006; Santos et al., 2013). Usually, the amount of fluid inclusions in quartz is related to its opacity (Fujiwara et al., 2015; Santos et al., 2013), which can be used to grade the samples in order to obtain a better material quality. Quartz resources with such characteristics are rare and their exploitation and processing are very costly (Götze, 2009; Haus et al., 2012; Santos et al., 2015). Often, companies start from less pure raw materials and use industrial processing to achieve the desired chemical purity. Such processing commonly involves acid leaching using HF and other hazardous materials (Li et al., 2010). The higher the amount of impurities in the raw material, the more expensive and environmentally damaging is the purifying process. Some chemical impurities, as Al, Ti and Ge, substitute Si atoms in the quartz lattice and are much harder to be removed (Gotze et al., 2004; Romanelli et al., 2012), than Na, Ca and K that are often located in fluid inclusions (Götze, 2009). As a result, the chemical composition of the raw material, that is, the abundance and characteristics of its impurities, is a key factor in determining the economic potential of the quartz resource.

Moreover, several procedures are followed to remove the contaminants from the quartz sand. These contaminants or mineral impurities, as previously described are chromite and titanium oxides. Iron may be present as individual particle of iron oxide or sulphides, or as a coating on the surface of sand grain. The free iron particles can be removed by using several techniques

such as gravity separation, magnetic separation or floating. However, the more challenging is to remove the iron staining which involve the environmentally unfriendly methods such as hot or cold leaching in sulphuric acid. Another method to remove iron staining is by attrition scrubbing (GWP Consultants LLP, 2010). Separation of iron oxide along with heavy mineral content is normally achieved by using the gravity separation. Specifically, gravity separation by spirals is a widely used and cost-effective methods of separation of heavy minerals. In this method, the material flows through a spiral-shaped trough under the influence of gravity, causing high-density particles to migrate towards the inner section of the spiral, where they are collected in a concentric channel. This process can be repeated multiple times to achieve the desired reduction in heavy mineral content. To handle minerals, magnetic separation becomes more suitable and is also considered a more environmentally friendly separation method.

Once the quartz rich raw materials are cleaned and all contaminants are removed, the actual preparation for glass production begins. All the purified materials are carefully weighed and blended into a uniform batch that meets the specific composition required for the intended glass product. This batch mixture is typically consisting of silica sand, soda ash, limestone, and cullet which is then fed continuously into a high temperature melting furnace. To melt the composition and produce a homogenous result, the temperature of the furnace must be high enough for the glass batch to become liquid. The melting temperature of glass varies depending on its type, typically ranging from 1100 to 1500 °C. Different types of refractory materials are employed in furnace construction, selected according to their position within the tank and the temperatures they are required to endure. High temperatures are achieved through various energy sources, including gas, fuel, electricity, or a combination thereof. During the fining stage of glass production, the temperature is increased to reduce the viscosity of the melt, allowing any remaining gases to escape. This process takes place in a separate section of the furnace known as the fining tank. Due to the extremely high temperatures involved, which can reach up to 1,600 °C, conventional refractory materials are unsuitable, as they would deteriorate under such conditions and could introduce impurities, including unintended colorants, into the glass. This is the reason for employing platinum, a material virtually unaffected by hot glass.

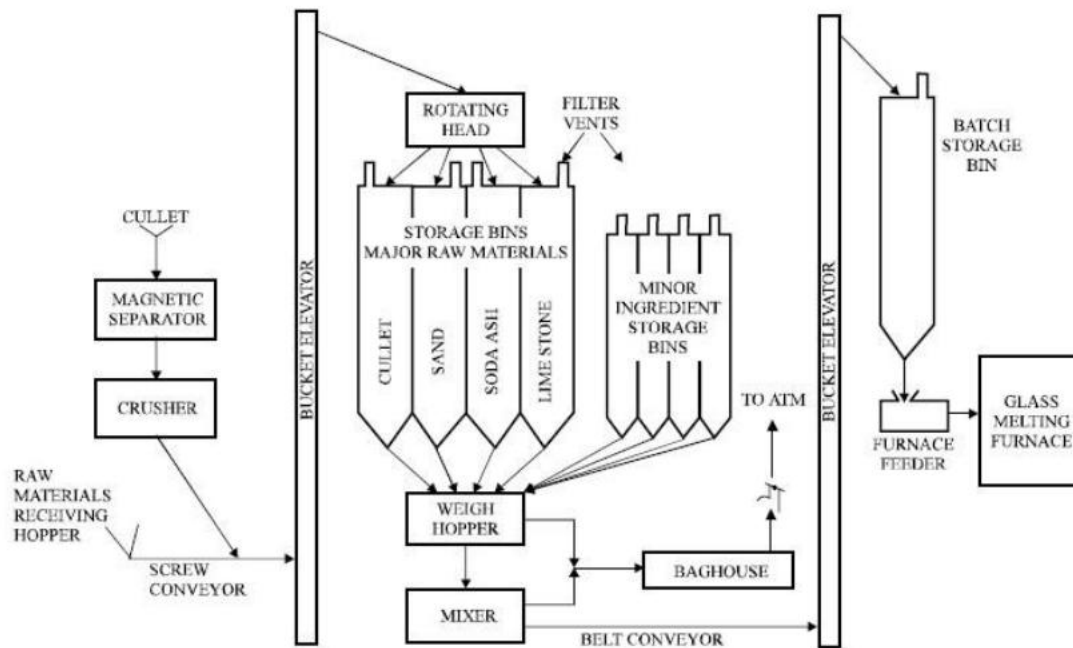


Figure 1.1 Schematic of a glass manufacturing plant process flow. Raw materials (sand, soda ash, limestone, cullet, and minor ingredients) are stored in bins, weighed, and mixed into a batch, which goes to the melting furnace. After melting and fining, the glass moves through forehearth or directly to the forming chamber. Finished glass is annealed and packed. (modified from the Corning website <https://www.corning.com/worldwide/en.html>)

In addition, to achieve the desired optical quality, ensuring complete homogeneity, the molten glass undergoes continuous mechanical stirring in a process known as *guinandage*, named after its inventor, Pierre-Louis Guinand. This continuous blending ensures a uniform composition and eliminates any residual inhomogeneities, preparing the glass for the subsequent forming processes. After refining, the molten glass exits the furnace and is shaped into the desired products through various forming techniques, including pressing, blowing, pressing-and-blowing, drawing, rolling, or floating. Pressing and blowing are performed mechanically using blank molds and glass sections, known as *gobs*, cut by a set of shears. In the drawing process, molten glass is pulled upward in a sheet through rollers, with the sheet thickness determined by the draw speed and draw-bar configuration. The rolling process is similar, but the glass is drawn horizontally over plain or patterned rollers, and for plate glass, subsequent grinding and polishing are required. The finished glass then undergoes additional finishing operations, such as decorating or coating, followed by annealing to relieve internal stresses. Each product is inspected for quality and prepared for shipment, while any defective or undesirable glass is returned to the batch plant to be recycled as cullet.

1.2 Brief History and Evolution of Glass Production

The discovery of glass occurred very likely by chance when objects made from crushed quartz and subjected to a surface treatment with an alkaline ligand (faience) were excessively heated; the first glass objects were produced in Mesopotamia before 1500 B.C (Moretti & Hreglich, 2013a). Glass industry, like other production industries, initiated in western Asia (Mesopotamia and Syria), during the 16th century B.C. Later when this region was conquered by Pharaoh Tuthmosis III dynasty (1505–1450 B.C.), glassmaking was also started in Egypt, where this technique flourished until the 11th century B.C (Moretti & Hreglich, 2013a). But during 11th to 4th century a long period of decline occurred in which almost no vases were produced in Egypt.

On the other hand, in Mesopotamia an era of productive recovery took place from the 9th century to the 6th century B.C., which was the times of Assyrian and Babylonian Empires.

This technique continued through the Persian Achaemenian period, until the fourth century B.C. This was that period when the lands of Macedonia were conquered by Great Alexander and spread Greek techniques, ideas and culture throughout Mesopotamia region and farther East. Since as early as the seventh century B.C., the glass making activity was expanded from western Asia to the eastern and central Mediterranean regions including the establishment of major glass centre in Rhodes, Etruria and Istria, near Italy (Brill & Rising, 1999). The creation in these Mediterranean centres for glass production has been reported and emphasize by many authors (Grose, 1977, 1983; Isings, 1957; McCann, 1987).

Therefore, it is obvious that the earliest glassmaking sites were established in locations where silica sand was readily available. Most of these sites were located along the Syrian Palestinian coast, between Akko (called Ptolemais and Acri) and Tyro today's regions of Sidon and Alexandria in Egypt, which was ancient capital of the Ptolemaic Kingdom. Since the mid first century B.C., new sites were also established near Rome. The very first and prime Syrian region where a specific type of sand was found at the mouth of river Belus (recently called Naaman river which flows into Haifa Bay). For the best results and to obtain workable glass, this sand was the particularly very suitable when it was added to a fluxing agent. In this way, the glass making technique was developed very rapidly in that region. Furthermore, the region of Sidon (now region of Lebanon) was very famous in the production of blown, engraved and polished glass, also to produce mirrors and many other glass objects. Moreover, some glass makers on the Syrian coast (Ennion and Artas) had moved to establish glass making technique in Italy.

Later from the literature, Pliny acknowledges that in more recent times, sand from the Volturnus River had been used in Italy for glass production. This sand was gathered for curing between the region of Cumae and Liternum (now Campania). The crushed sand was sieved and later mixed with nitre in a ratio one part to three, in weight or volume. By treating in an appropriate furnace, a mass was obtained and called hammonitrum (the equivalent of a frit). After a successive fusion, the substance became beautiful white glass (Moretti & Hreglich, 2013b). Pliny then also explains that the sand was handled according to the same techniques in both Gaul and Spain.

During the second half of 16th century, a manuscript known as *Ricettario anonimo del '500* was published which was an important document regarding the glass production evolution (Moretti & Toninato, 2001). This useful text provides around 105 recipes regarding the ash treatment to produce frit and crystal glass, crystalline and ordinary glass, lead glass and white opaque glass. This manuscript also contains information about numerous techniques and recipes to produce chalcedony glass, and glass for simulated stones, mosaic and enamels. Many of the techniques in Muranese books are similar and was also found in Neri's book, which indicates the presence of a common source (Moretti & Hreglich, 2013b). In above said recipes the raw materials utilized include soda ash (*allume catino*) or ash derived from other unspecified plants. After purification and burning process, the purified tartar was supplemented to form the 'salt of glass', which acted as the flux for quartz (obtained by crushing pebbles from the Ticino River), used to make *cristallo in tutta perfezione*. Once the glass was melted, it was poured and dipped into water and then melted again. Ordinary glass was obtained from a frit made with non-treated, non-purified ash and quartz powder. Lead glass was made with litharge and quartz powder. By adding lead and tin calx or tin calx to crystal or ordinary glass frit, white opaque glass was obtained through melting. It was then poured into water and re-melted. Therefore, from all the above literature, after 16th century to 19th century similar procedures was followed for glass production.

In the 20th century, the chemical industry was characterized by rapid and uncontrollable growth which rapidly gave rise to a drastic change in the types of raw materials that had been used until then in glass manufacturing. Most of the conventional raw materials were gradually replaced by very pure products obtained by synthesis. These synthetic raw materials were characterized by their consistent composition and were produced in large quantities in special industrial plants. All these important innovations have made the work of glassmakers easier. In



Figure 1.2 A black and white sketch of the first furnace used for glass making. Adapted from Moretti & Hreglich (2013b).

particular, it is worthwhile mentioning the deposits of highly pure silica sands located in the regions of Fontainebleau and Nemour (south of Paris) and along the border between France and Belgium, as well as calcareous silica sand from a mine situated north of the town of Pola (Istria), used by glassmakers in Murano from the end of the eighteenth century until the first decades of the twentieth century (Moretti & Hreglich, 2013b). In the beginning of the 20th century, the recipes of glass (glass packaging and flat glass), in which high levels of alumina and silica are needed, feldspar and nepheline were increasingly introduced as natural, cheaper products. Since their structure contains silica, alumina, sodium and/or potassium, they can simultaneously act as vitrifying agent, stabilizer and flux. The Solvay process, established in 1861, was used to make sodium carbonate (synthetic soda) from calcium carbonate, ammonia and sodium chloride. With the development of this process, the glass industry began to use this compound as a fluxing raw material instead of plant ashes. During the first part of the 19th century, the role played by modifier/stabilizer oxides in glass manufacturing was finally understood. Therefore, natural raw materials containing calcium, magnesium and barium oxides were increasingly used. Limestone and dolomite are easily available in large deposits scattered all over the Europe, began to appear in significant quantities in glass recipes. In 19th century glass production, new colours appeared, such as uranium yellow, which was produced

in Bohemia from 1830 onwards, thanks to the addition of uranium oxide to the batch. During the second half of the 19th century, glassmakers started to use metallic selenium associated with cadmium sulphide to obtain so-called Imperial red.

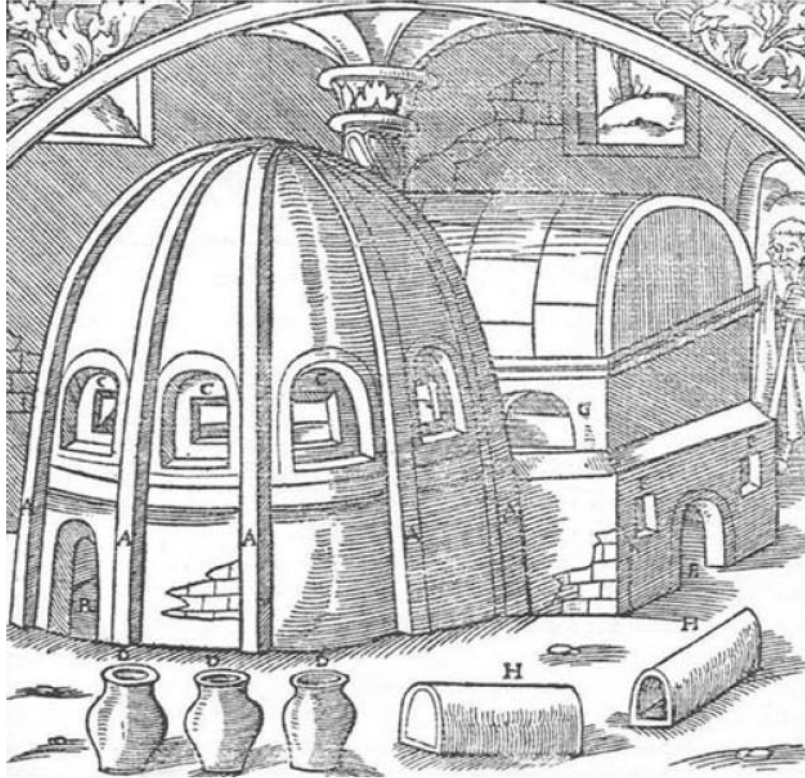


Figure 1.3 Black and white sketch of second and third furnace for glass making Adapted from . Adapted from Moretti & Hreglich (2013b).

During late 20th century and earlier 21st century there is a transformative period in glass manufacturing, which results by advancements in synthetic raw materials and industrial processes. The shift from traditional to highly innovative pure and consistent inputs boosted efficiency and developed the range of glass properties and colours. These innovations significantly modernized production and widen the potential for technical and decorative glassmaking.

1.3 Quartz rich silica sand deposits in Italy

World production of quartz (including quartzite and other high silica industrial sands) is estimated to be around 315 Mt per year (Brown et al., 2016; Reichl et al., 2018). The major producers are the US (about 38% of the world total), Turkey (15 Mt), Malaysia (10 Mt), India (8.5 Mt), Brazil (7 Mt), Korea (4.5 Mt), and Australia (3 Mt). The extraction of silica sand in

Japan, Mexico, Canada, New Zealand, South Africa, and Iran is between 2 and 3 Mt each. The United Kingdom contributes for 4 Mt per year of silica sand. Silica sand cost was between 30 € and 200 € per ton over the period 2012–2016 (EC, 2017). At EU level high grade silica (>99% SiO₂) is produced in the Netherlands, Italy, France, Germany, Bulgaria, Spain, Poland, Belgium, and the Czech Republic.

1.3.1 Known Quarries in operation

1.3.1.1 Sondalo quartz mine

The mineral mined in Sondalo consists of compact quartz that varies in mass from transparent to grey to milky white. Chemically, Sondalo quartz is characterized by a high natural purity, resulting in SiO₂ contents in the rough materials always exceeding 99%. Mineralogically, the typical paragenesis consists solely of quartz without accessory phases; exceptionally, the presence of microscopic aggregates of feldspar, chlorite, muscovite, and tourmaline has been recognized. In some areas, generally distributed along bands adjacent to the contacts, impurities can be observed within the mass. These consist mainly of small deposits of oxides, iron hydroxides, and amber-yellow silts that appear to settle along fracture zones, creating widespread coloured patinas on the mineral.

Minerali Industriali is particularly proud of the Sondalo quartz mine, in the province of Sondrio, opened in the mid-1960s with “open pit” excavation methods. Then, since the mid-90s the business has moved underground with undoubted landscape and environmental advantages. The extracted mineral has a silica content of over 99%: about 33,000 tons per year are extracted for the grinding plants of Bernate Ticino (MI) and Cacciano di Masserano (BI) for use in the E- industry. stone, sanitary ceramics, ceramic paint factories and as a raw material for the ferroalloy sector.

1.3.1.2 Monte Bracco Area

The Monte Bracco area (western Alps, northern Italy) is well known for the "Bargiolina" quartzite, a stone that has been exploited in slabs at least since the 13th century, used as internal and external facing, especially in the Baroque (Rodeghiero et al., 2020). The quarries are located mainly on the top of the Monte Bracco, geologically pertaining to the Dora-Maira Massif, a crystalline massif of the Penninic Domain (Palaeozoic basement and a thin Mesozoic cover). The quartzites occur in sub-parallel lenses (thickness between 2 and 10 m), hosted by ortho- and paragneiss, locally strongly altered in clayey material (kaolinization) (Compagnoni et al., 2012; Rodeghiero et al., 2020). The quartzite varieties are characterized by a fine and homeoblastic grain size, a granular - lepidoblastic texture, with regular spaced schistosity, and

the main rock-forming minerals are quartz (70 - 90 wt.%), phengite (up to 15 wt.%), K-feldspar (orthoclase, 5 - 10 wt.%, frequently altered in kaolinite) and traces of albite, chlorite and accessory minerals. The quartzitic bodies have been quarried by different companies.

1.3.1.3 Snive opencast Quarry

Snive quartzite quarries are the series of quarry located at Roaschia, Robilante and Roccavione, Province of Cuneo, north-western Italy. The “Snive” opencast quarry is the biggest Italian quarry for the extraction of quartzite focused on the production of silica-rich sand for the glass industry. The yearly quarry run amounts to about 1-1.5 Mt. The raw material is hauled downslope to the Robilante industrial plant via a 7 km-long conveyor belt where it is crushed and sifted to give the final product. At Snive quarry, the geological assistance is given by the client company, Sibelco Italia SPA.

1.3.1.4 Melfi Quarries

Pilkington Italia is the part of the NSG Group, which owns and operates a specialized silica sand quarry located at Contrada Pisciolio in Melfi, Italy. This open-pit mine extracts and mills sandstone to supply silica sand to different glass-producing facilities. The mined sandstone is crushed on-site using shredding and milling equipment to produce high-grade silica sand before being transported to sites for glass making.

1.3.1.5 Numidian Quartz rich sandstone

The Numidian sandstones are considered the most prevalent sedimentary events in the Peri-Mediterranean Chains (Fornelli & Micheletti, 2021a). These sandstones represent the Early-Middle Miocene depositional framework of the Mediterranean foreland basin systems from Southern Spain (Betics), Northern Africa (Rif-Tell Chain), Sicily to Southern Apennines (Italy). The depositional age shifts from Early Miocene in the Betics, North Africa and Sicily to Early Langhian in the Southern Apennines (Belayouni et al., 2013; Pinter et al., 2016). The Numidian sandstones occurred in layers with kaolinitic clays and were deposited mainly in deep- marine depositional systems (Critelli, 2018; Critelli et al., 2017; Fornelli & Micheletti, 2021a). These deposits mainly consist of sediments which are derived from gravity-flows and are characterized by peculiar ultra-mature quartz-arenites containing mainly well-rounded monocrystalline quartz grains. These textural and mineralogical features make these sandstones ideal for use as raw materials in several industrial processes such as glass industry (Fornelli & Micheletti, 2021a).

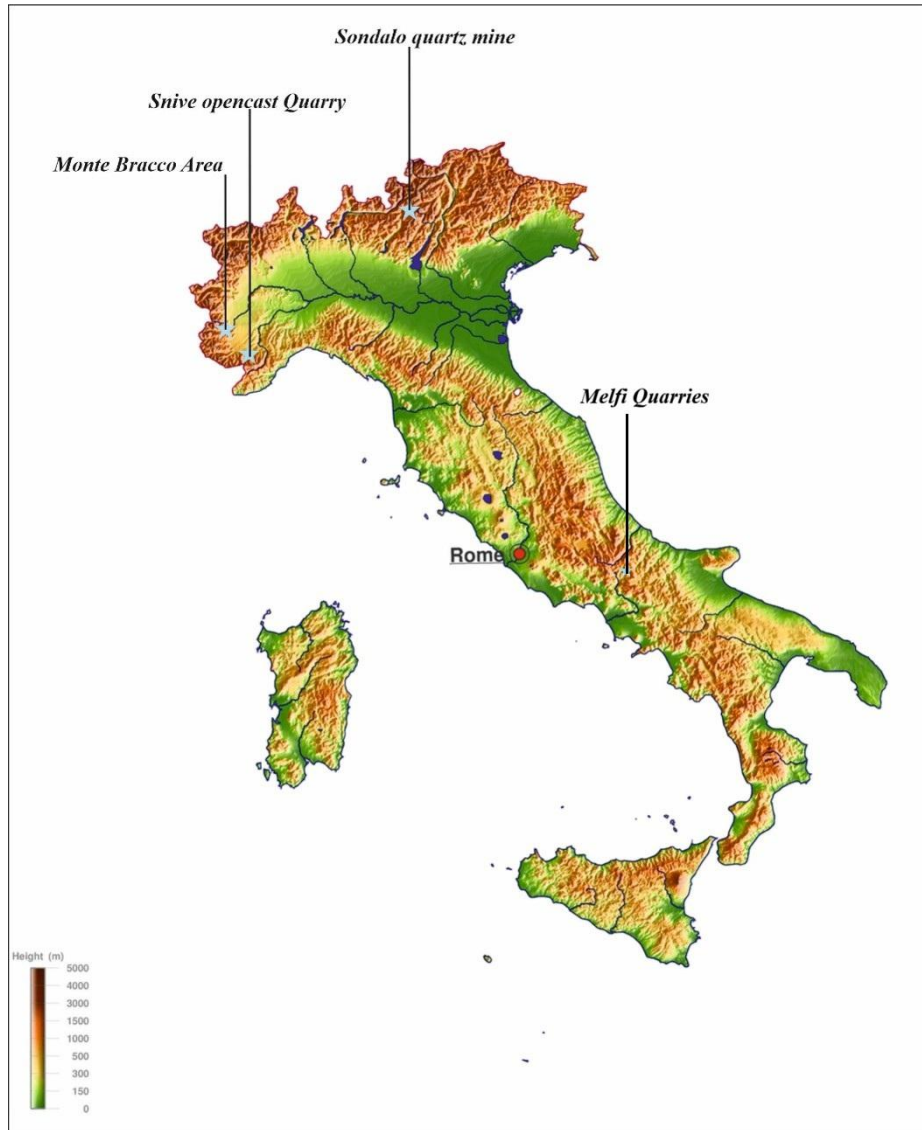


Figure 1.4 Topographic map of Italy illustrating the principal quartz-rich sand quarry sites, marked by star symbols

1.4 Exports

In 2023, Italy exported \$6.94M of quartz rich sands, making it the 27th largest exporter of quartz rich sands (out of 152) in the world. During the same year, quartz rich sands were the 2,993rd most exported product (out of 4,565) in Italy. In 2023, the main destinations of Italy's quartz rich silica sands exports were to Portugal (\$1.6M) worth, Spain (\$615k), France (\$428k), Switzerland (\$393k), and Russia (\$335k). The fastest growing markets for quartz rich silica sands exports from Italy between 2022 and 2023 were: Portugal (\$1.52M), Russia (\$114k), and Romania (\$81.9k) (AJG Simoes & CA Hidalgo, 2011).

1.5 Imports

In 2023, Italy imported \$77.1M of quartz rich silica sands, becoming the 5th largest importer (out of 205) in the world. During the same year, quartz rich silica sands were the 1,107th most imported product (out of 4,542) in Italy. In 2023, Italy imported quartz rich silica sand primarily from: Egypt (\$17.9M), Germany (\$15M), France (\$13.5M), Portugal (\$11.8M), and Tunisia (\$5.42M). The fastest growing origins for quartz rich silica sand imports in Italy between 2022 and 2023 were: Egypt (\$9.56M), Spain (\$4.53M), and Germany(\$3.83M) (AJG Simoes & CA Hidalgo, 2011).

1.6 Research Aims and Objectives

This research project aims to define advance mineralogical techniques which help in production of glass using sand very rich quartz. The following are the main objective of this study,

- Mineralogical investigation of the material in currently active quarries.
- Control of the mineralogy of the sands entering the industrial plants scattered throughout the territory.
- Development of a rapid emergency intervention protocol to recognize and isolate any contaminants before they enter the production process.
- Creation of fixed and mobile laboratories equipped with a kit for preparing and validating the quality of incoming raw materials for the Verallia Italia plants.
- Staff training through knowledge transfer and dissemination and sharing actions.
- Identification of new primary reservoirs, in different geological contexts, to assess the availability and presence of potential new quartz sand reservoirs.

MATERIALS AND METHODS

2. MATERIALS AND METHODS

2.1 Materials

During this project, different sets of samples were received from industry for detailed analysis. This included quartz rich sand as the primary raw material, several final stage glass embedded impurities and few raw silica sand samples from quarry for analysis. The complete list of received samples analysed for this study are listed below:

- 1) Five different samples of quartz rich sands are received from two different Verallia plants (Gazzo V.se and Dego). All these samples are the raw material used in different plants of Verallia Italia. Detail of these samples are below.
 - i. **SAB-2**: Silica sand from SIBELCO supplier (the most used in our production).
 - ii. **SBT**: Silica sand F12 from QUARZWERKE supplier (“German” sand low iron content).
 - iii. **Port 40/45**: Silica sand from SASIL supplier (“Portuguese” sand very low iron content – S40-45FL).
 - iv. **TS-2**: Silica sand from SASIL supplier (“Tunisian” sand low iron content).
 - v. **SRD 4V**: Feldspar sand from Sardinia provided by MAFFEI SARDA SILICATI (sand from Sardinia with low iron content).
- 2) Many glass cut pieces were analysed during this project time to time (shown in Fig 4.2). These impurity bearing glass pieces were extracted from the main products (glass bottles) by cutting.
 - i. 23 glass pieces were collected, numbered from 1 to 23. The impurities contained in these glass pieces were previously used as reference to compare their physical appearance with newly recorded impurities and for naming them.
 - ii. A set of 20 glass pieces was also collected which was recorded as the daily impurities.
 - iii. A set of another 17 glass pieces containing impurities was received from industry.
- 3) Two crushed powdered samples i.e. V1 and V2 were collected during the visit to company. These samples are from the crushing procedure of the glass cullet.
- 4) Another two raw material samples were collected following the cleaning procedure applied to the raw feed material. These samples were the quartz rich sand.

- i. **S1:** the material corresponds to the input feed for the wet process, obtained after the primary (jaw crusher), secondary (cone crusher), and tertiary (cone crusher) crushing.
- ii. **S2:** the material comes from the downstream of a fourth grinding stage and after classification processes and washing, the sample was taken upstream of a deferrization process with a magnetic separator (Eriez).

2.2 Methodologies

2.2.1 Gravimetric separation

The sand introduced into the production process needs to check and deploy quality control protocols. Therefore, different quantitative approaches are necessary for the identification and elimination of accessory minerals other than quartz. These accessory mineral (trace minerals) in sand can be quantified by using gravimetric separation techniques. This separation technique used in provenance studies can be modified and applied for applications in the industry improving the ability to identify heavy minerals as potential impurities and contaminants.

Therefore, by using gravimetric separation technique the quantitative analysis was carried out to identify the mineralogy of collected samples from different quarries and used in plants of Verallia Italia. By using this method, the 15-500 μ m fraction of grains was selected to encompass a wide sediment size distribution (Garzanti et al., 2009).

The amount of sample needed for heavy-mineral separation depends on several factors, including expected heavy-mineral concentration, grain size, sorting, and type of study. In this part of the study, this technique is employed to estimate and determine the amount of heavy mineral as the impurities in the specific sand samples and ultimately to evaluate the overall quality and composition of the material. By obtaining quantitative results for each sample, the study provides reliable basis for understanding the impurity level in the specific sample.

Preparation of samples

A few sand samples delivered by Verallia was received as wet. All these wet samples were transferred to the aluminium tray and left for drying in oven at temperature of 40°C. Though, the amount of each sample received was too large, so the splitting techniques was used to get the reduced representative amount of the sample. The Parfenoff's technique (Parfenoff et al., 1970) and riffle box splitter was used efficiently for producing the representative smaller portion for analysis. Considering the expected concentration of heavy minerals in each sample, the specific amount of material used was adapted according to the sample type, following Provenances Laboratory standards(Andò, 2020). Therefore, about 30g of representative sample, with the

exception of S1 and S2, for which 77.8g and 35.3g were used, respectively. Strating from sample of ~30 g fractions of $<15\mu\text{m}$, $15\text{-}500\mu\text{m}$, and $>500\mu\text{m}$ was obtained by using nylon and steel sieve of $5\mu\text{m}$ and $15\mu\text{m}$ respectively. By using cleaned $500\mu\text{m}$ steel sieve mounted onto a sieve bottom pan with drainage outlet, the grains $>500\mu\text{m}$ was retained on the sieve while the $<500\mu\text{m}$ grains passes through the sieve and from drainage outlet collected into the beaker. The whole setting of this apparatus is shown in Fig 2.1.

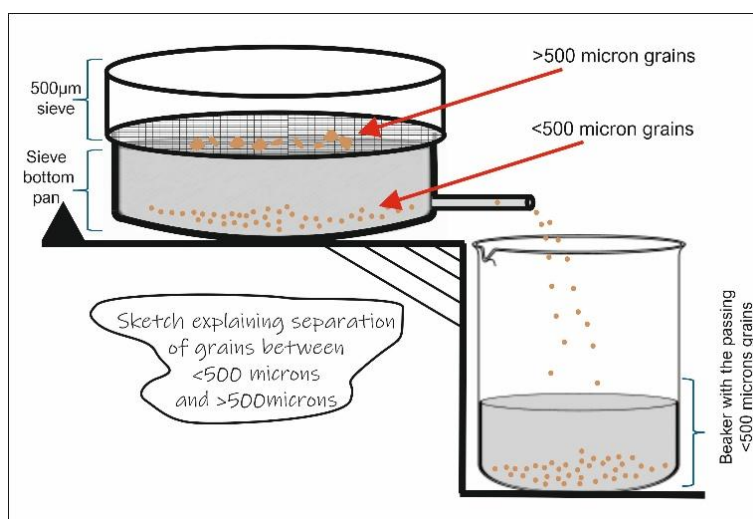


Figure 2.1 Schematic representation of the apparatus employed in the gravimetric technique for separating grain sizes. Particles $<500\mu\text{m}$ pass through the sieve and are collected in a beaker beneath the bottom pan, whereas particles $>500\mu\text{m}$ are retained on the sieve.

The retained grains $>500\mu\text{m}$ were collected in filter paper and kept in oven for drying. Once dried this grain fraction was kept in container and weight was noted on the sheet. On the other hand, the entire amount of $<500\mu\text{m}$ grains was collected from bottom pan into the beaker. This labelled beaker with sample number was left to settle overnight. After all the grains was settled, most of the water was siphoned off with a little tube by using the basic principle of Pascal's communicating vessels. Once some water left the subsequent $15\mu\text{m}$ wet sieving was carried out by using handmade sieve of $15\mu\text{m}$ mesh. The prepared sieve (Fig 2.3) was then placed in a funnel sustained by a metal rack, centred above a beaker with labelled sample number. The sieving process was speeded by continuously and gently stirring the finger to prevent clogging of sieve and helps passing the grains more effectively. This process was repeated again and again with the help of supplementary beaker to let the water pass through and clean the net. Finally, after this multi phased procedures, the cleaned $15\text{-}500\mu\text{m}$ fraction was obtained. Thus, obtained fraction was transferred on the labelled filter paper for drying and further use. The fraction of $15\text{-}500\mu\text{m}$ is the desired fraction for the identification of heavy minerals. The

passing $<15\mu\text{m}$ fraction was collected in beaker and left to settle. The excess water was removed using the same principle of communicating vessels and then beaker left in oven until the grains completely dried. The dried $<15\mu\text{m}$ fraction was weighted and noted on the sheet.

Centrifuge separation

Dry samples were put into the labelled test tubes. The sample volume should be in proportion to the capacity of the test tube. Then the sample were mixed with Sodium polytungstate, (a heavy liquid at density 2.90g/cm^3) and tubes were shaken thoroughly. To maintain the centrifuge in equilibrium, all the tubes were weighted equally before placing in the centrifuge machine. Our laboratory was equipped with centrifuge with four positions so, we placed four tubes in one session. According to the sample type (sand) and selected grain size window (i.e. $15\text{-}500\mu\text{m}$) we allowed 2000 and 3000 rpm and three minutes configuration (Fig 2.2). After centrifugation, the tubes contained heavy minerals settled at the bottom and light minerals remaining at the top. While the centrifuge was in operation, two set of funnels with beaker and filter paper was arranged for each sample (configuration shown in figure). Each filter paper was labelled with sample number. A plastic bucket was prepared, filled with appropriate liquid nitrogen and then test tube was dipped into that bucket keeping the tubes in vertical positions.

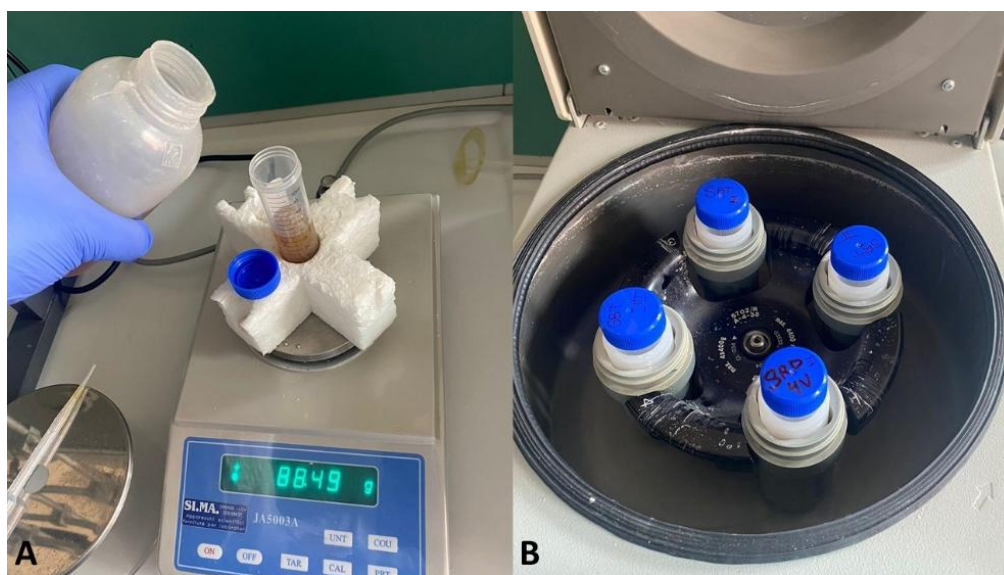


Figure 2.2 (A) Addition of Sodium polytungstate to a conical tube containing a sample on a weighing scale. (B) Conical tubes prepared and placed in the centrifuge for centrifugation.

After couple of minutes, the lower part of the test tube, which contains the heavy fraction was frozen (Fig 2.3). The non-frozen liquid, which contains light fraction was recovered in the set of corresponding samples filter papers, prepared for light mineral fraction. Also, the lower part

of test tube was defrosted by adding deionized water. Once the heavy fraction was unfrozen, it was recovered in the set of filter paper reserved for heavy minerals (Fig 2.3). Each fraction was cleaned with distilled water until the water in the beaker appeared clear, indicating that the sample has been cleaned. Later the labelled filter papers containing the fractions was folded, closed with a peg, and placed in oven for drying overnight with 40-50°C. The diluted liquid can be re-used after water evaporation.

Preparation for Microscopic Analyses

Once the fractions were dried, after weighting and recording each fraction, the next step was to make the thin sections of heavy minerals fractions. Generally, the recovered amount of heavy fraction is much greater than what is needed to prepare a grain mount. But in most of our samples, the amount of heavy minerals recovered was just sufficient to prepare a thin section, with none remaining. In case of sample S1 and S2 the amount of heavy minerals recorded was too abundant to be mounted on the microscope slide. So, the splitting was necessary using the riffle micro-splitter. The selected heavy fraction was then poured on the labelled small piece of white paper and then folded to prevent contamination. Meanwhile, the hot plate covered by aluminium foil was warmed up to approx. 130°C. The glass slides were cleaned with sanitary tissue paper by using denatured alcohol, to remove any traces of dust and micro fragments. After cleaning, the glass slide was placed on the preheated digital hot plate along with glass cover slip and toothpick was used for pushing and relocation. A drop of Canada balsam was placed on the glass slide with the help of spatula and remain for couple of minutes to warm enough. Once the Canada balsam was heated appropriately, the folded paper containing the heavy minerals was poured out with all grains within the Canada balsam. The toothpick was used in concentric circle to evenly spread all the grains within Canada balsam. Overlapping of grains should be avoided for a good optical analysis under the microscope. With the help of another toothpick, the cover slip was moved to edge of hotplate and then overturned on to the glass slide. After a couple of minutes, the Canada balsam was polymerized and was dip into the normal tap water for few minutes. Finally, the glass slide with the grain mount was properly labelled, and any residual Canada balsam was cleaned off using alcohol and paper.

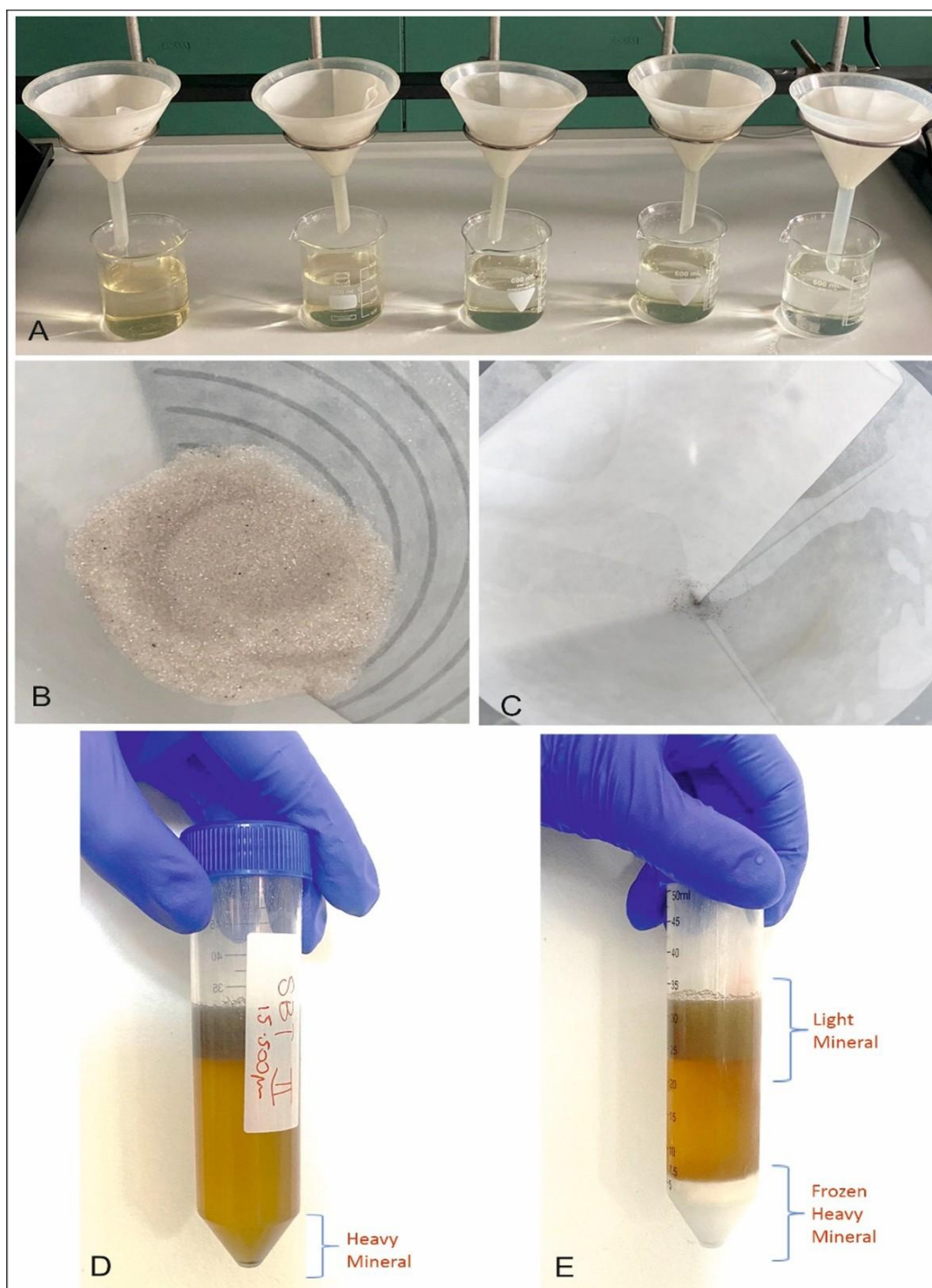


Figure 2.3 (A) Apparatus use for the recovery of the heavy mineral fraction by washing with distilled water. (B) Cleaned light mineral fraction after washing with water. (C) Cleaned heavy mineral fraction after washing with distilled water. (D) The conical tube after centrifuge separation, showing the heavy mineral fraction settled at the bottom. (E) The conic tube after partial freezing of the heavy minerals fraction using liquid nitrogen.

Microscopic identification

In 1808, the polarization of light was observed and study by Étienne Louis Malus, a French physicist and mathematician. Later in 1828, William Nicol's invented the Nicol prism which was the first step in the development of polarizing microscope. In 1830, the first ever complete polarizing microscope was built by Giovanni Battista Amici, and later the microscope was adapted specifically for mineralogy, or petrography, by Rudolf Fuess in 1875. Today, polarizing microscopes use more modern polarizing filters instead of the original prisms to study anisotropic materials like minerals and living cells. Many articles are published to make the identification of minerals by using their optical properties (Mange & Wright, 2007; Mange & Maurer, 1992; Parfenoff et al., 1970; Teertstra, 2005; Tröger, 1956). In addition to traditional publications, numerous online databases are now available that provide detailed information on the properties of minerals, accompanied by extensive references for individual species (Hudson Institute of Mineralogy, 2025).

In this study each mineral species can be confidently recognized based on a diagnostic combination of distinctive optical features for individual mineral. Under the polarizing microscope, a series of observations was conducted using both plane-polarized light (one Nicol) and cross-polarized light (two Nicols). With one Nicol, the external morphology and internal characteristics of the mineral grains are examined, including their form, colour, degree of pleochroism, relief, cleavage, and the presence of inclusions or alteration features. These attributes provide valuable clues for identification and assessment of the minerals. When observed with two Nicols, additional optical properties become evident, such as birefringence, interference colours, extinction angle, and elongation, all of which contribute to a more precise determination of mineral identity. Furthermore, the use of convergent light allows the observation of interference figures, which are essential for determining the optical sign (positive or negative) and optic axial angle, thereby completing the optical characterization of each mineral species. Therefore, by using all these optical properties, the minerals in this study were accurately identified and classified.

Point counting

To estimate the relative abundance of heavy minerals in a specific sample, different grain counting techniques are used i.e. Fleet methods, Line counting, Area or ribbon method, and point counting. In point counting techniques the thin section was moved following a grid of equally spaced points along equally spaced linear traverse (Carver, 1971; Garzanti & Andò, 2019). By using this method, the probability of a grain being hit by the cross hair along this grid is proportional to its visible area. In this way the areal percentage of various component

of slides was obtained, which are equivalent to volume percentage (Chayes, 1954). Furthermore, it is important to ensure that the grid spacing needs to be large enough so that the grains are not counted twice. In this study we applied the same technique and used the fixed spacing of 200microns the grains hit by the microscope crosshair was identified and counted.

2.2.2 Raman spectroscopy

Fundamentals

Raman spectroscopy is based on inelastic scattering of light by matter in its solid, liquid, or gas state (Frezzotti et al., 2012). Monochromatic light scattered by matter contains radiations with frequencies different from the exciting light. This effect was first predicted and study by (Smekal, 1923). Later this phenomenon was demonstrated by (Raman, 1928) and named after him. This discovery of innovative optical scattering phenomenon eligible him for Nobel prize in physics in 1930.

This phenomenon had come into notice of Raman when he observed the scattered light in liquids, which had energy greater than the incoming light. So, this innovative observation assured him that he was in presence of a new light scattering effect (Raman & Krishnan, 1928). Whereas the same phenomenon was noticed by (Landsberg & Mandelstam, 1928) independently in Moscow.

Quantum mechanical principles are considered to explain the Raman scattering in simplest way, as the interaction of photons with molecules through an energy transfer mechanism (Davis & Oliver, 1972; Karr, 1975). Principally, a molecule has different vibrational energy levels, the ground state $n=0$, and the excited states $n=1$, $n=2$, $n=3$ etc., which are separated by a quantum of energy:

$$\Delta E = h \nu_m$$

where h is the Plank's constant and ν_m is the frequency of the molecular vibration.

The incident visible light ($\lambda=400\text{--}750$ nm) with energy ν_l induces transitions to virtual vibrational energy levels in molecules. However, a virtual level is not considered to be an actual energy level of the molecule while it is generated when light photons interact with the molecule, raising its energy (Frezzotti et al., 2012). Therefore, this virtual level is unstable, and light is instantaneously released as scattered radiation. Returning to the initial state occurs by emitting light of frequency.

$$\nu_l, \quad \nu_l - \nu_m, \quad \text{and} \quad \nu_l + \nu_m.$$

The concept is illustrated in (Fig 2.4). The Rayleigh or elastic scattering occurs when the transition starts and finishes at the same vibrational energy level without loss of energy (i.e.,

no frequency change; ν_l). Inelastic scattering (Raman effect) induces a change to lower ($\nu_l - \nu_m$) and higher ($\nu_l + \nu_m$) frequencies in scattered light, which are known as Stokes and anti-Stokes lines, with ν_m representing a fundamental rotational, vibrational or lattice frequency of the molecule. Rayleigh scattering can account for most of the light scattered by molecules, being the Raman effect extremely weak in the order of some 10^{-6} - 10^{-8} of incident photons and variable, as the intensity of the Raman scattering is proportional to the fourth power of the frequency of the incident light.

Raman spectroscopy is the measurement of the photons appearing from inelastic (Raman) scattering of light. A Raman spectrum is the plot of light intensity expressed as arbitrary units, or counts, versus the frequency of scattered light (i.e., Raman vibrational modes) in frequency units (wavenumbers $\nu = \frac{v}{c} = \frac{1}{\lambda}$ in cm^{-1} , where c is the velocity of light). Typically, only Stokes Raman scattered frequencies are presented since they have the same energy but are about 10 times more frequent than their anti-Stokes counterparts. The Rayleigh scattered frequency (i.e., light-source wavenumber) lies at 0 cm^{-1} and Raman frequencies are expressed as relative wavenumbers, or Raman shifts. On this scale, frequencies correspond to the energy levels of different molecular vibrations and are independent from the wavelength of the light source. A spectrum comprises one or more bands which reflect the vibrational energies of the molecules within the analysed sample; these in turn are related to the nature of the bonding. Main molecular vibrations include stretching and bending modes, stretching frequencies being generally higher than bending frequencies. For a normal mode of vibration to be Raman active, it should produce a change in the polarizability of the molecule. The “selection rules” for Raman scattering depend on:

- 1) the creation of an induced dipole in the molecule (polarization)
- 2) the modification of the dipole by a molecular vibration
- 3) the successive scattering of a photon from the modified dipole (McMillan & Hess, 1988).

In Raman spectroscopy, the primarily instrumental setup requires a source of monochromatic light, generally a laser, focused on a sample (solid, liquid, or gaseous); the light is scattered, collected at a 90° or 180° angle, and analysed by a detector (Fig. 2.4). In the first dispersive Raman spectrometers, the sun or a mercury lamp was used as the exciting source with a prism monochromator as the light disperser, and a photographic film as detector (Colthup et al., 1975). In modern commercial instruments, polarized laser light sources in the UV, visible, and IR are used to excite molecular samples, because of the high intensity and narrow bandwidth

of wavelengths that are emitted (monochromaticity), and multi-channel charge-coupled devices (CCD) are generally used as detectors. Their combination, together with notch holographic filters to eliminate the Rayleigh line, results in more intense Raman scatter, with considerably reduced measuring time in obtaining high signal to noise spectra (i.e., tens of seconds), and low detection limits. In simple words the laser excites the molecules to generate scattering. The choice of type of laser wavelength impacts the performance of the spectrometer. Generally, the optical power of the laser line and the efficiency of Raman CCD detectors tend to increase with decreasing wavelength (Frezzotti et al., 2012). However, the cost of the laser,

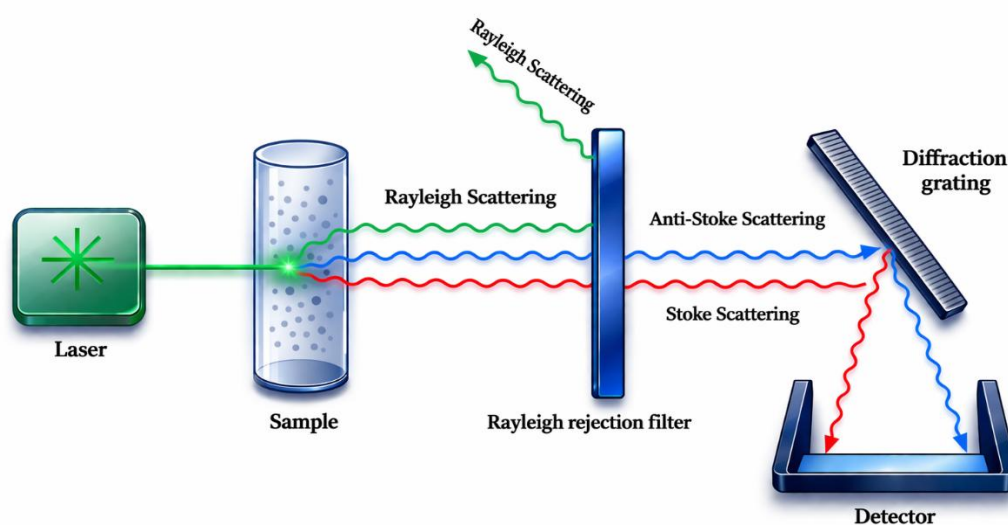


Figure 2.4 A schematic diagram illustrating the basic principle used in Raman spectrometer.

the likelihood of fluorescence, and the risk of sample heating increase as well. The most popular choices in laser are:

- (1) the green light which may be of Ar ion ($\lambda=514.5\text{nm}$) water or air-cooled or commonly used ($\lambda=532\text{nm}$),
- (2) the blue light Ar ion ($\lambda=488\text{ nm}$) air-cooled and
- (3) the red light He\Ne ($\lambda=632.8\text{ nm}$).

The fluorescence often overpowers or conceals the weak Raman features. Fluorescence interferes with Raman spectroscopy by producing a strong broadband signal that can obscure the much weaker Raman peaks. This fluorescence effect may usually is because of epoxy material used to embed or polish the rock sections. The fluorescence produced because of this effect can easily be resolved by using preferably the epoxies of non-fluorescent nature. Another reason of fluorescence produced during the mineral analysis is the presence of inclusions (e.g.,

hydrocarbons, Fe-bearing minerals). This type of fluorescence is much more difficult to cope with. Therefore, technically it is considered that, by increasing the wavelength of the light source is a way of overcoming fluorescence (Carey, 1999). Alternatively practical approach to minimize a fluorescent background is repeating the spectral accumulations for several times in order to bleach out the effect by protracted exposure to laser light (photo-bleaching) (Frezzotti et al., 2012). Interpretation of spectra is often challenging because the intensity of Raman scattering is greatly influenced by the orientation of the specific crystal lattice. This indicates that if there are some variations in crystal alignment than the significant changes are expected to observe in spectral features and ultimately more complicated to obtain reliable and comparable results. To tackle this problem, precise sample preparation, orientation control, and polarization studies are often required.

Once the spectra have been obtained, the next step is to analyse them to predict the possible mineral. This could be done by comparing the recorded spectra with the literature. For this purpose, the most used database is the RRUFF database. The RRUFF database was established in 2006 at Arizona State University by Robert Downs. RRUFF presently includes tens of thousands of spectra acquired at several different laser wavelengths from oriented and un-oriented samples (Downs, 2006). In this study, alongside the RUFF database, we also used another database established internally in the Laboratory of Provenance Studies at the University of Milano-Bicocca by Prof. Sergio Andò and Guido Pastore (Andò & Garzanti, 2014).

2.2.3 Granulometric Separation

The goal of granulometric analysis for unconsolidated sediments is to quantify the distribution of particle sizes within the sample. Initially the two samples i.e. S1 and S2 was received for granulometric analysis. Both samples were received as wet.

Drying

The decanted samples are placed in an oven (Fig. 16) for drying. Depending on the sediment type and the intended analysis, samples are dried for 24 to 48 hours at a temperature of 50°C to 60°C. A higher temperature should be avoided to prevent 'cooking' the sediment, especially in the case of clay-rich samples. Dried sediment may present a crust composed of fine baked sediments. This problem is often encountered. In this case, the crust must be very delicately broken down with a mortar and pestle. this is a delicate operation, as the risk is to create a finer sediment than the one initially present in the sample. To prevent this problem when the

sediment is very rich in clay, the drying temperature should not exceed 30°C. The drying time is then adapted, sometimes up to 72 hours.

Separating

Obtaining an appropriate amount of sample is crucial for accurate analysis. Since all our samples are sourced from the glass industry, they are received in bulk quantities (measured in kilograms), which are far larger than what is required for the intended analyses. Therefore, obtaining a truly representative portion from the bulk sample is critical.

In the laboratory of provenance studies, several methods are employed to ensure representative sampling. For large bulk samples, the Parfenoff method (Parfenoff et al., 1970) is commonly used. In this method, the dried sample is placed on a clean sheet of paper and thoroughly homogenized by rolling and folding the paper until a uniform cone of sediment is formed. The cone is then divided into four equal parts, and one quarter is taken for analysis while the remaining portions are stored. This procedure can be repeated as necessary until the desired sample quantity is obtained.

Weighing

Once the desired sample quantity is obtained, it is essential to record the total bulk weight by using a precision balance, which must be stabilized on a perfectly horizontal surface, tared, and protected from air movement. Another weighing step is performed when each sieve fraction is measured using a precision balance. All measurements are first recorded on paper and then transferred into a spreadsheet for statistical analysis.

Sieving

A sieve column consists of a stack of sieves, each with a progressively smaller mesh size, allowing for the separation of sediment by grain size. Typically, the finest sieves have a mesh size of 0.032 mm, while larger sieve size of 8mm. The sieve column is often placed in a sieve shaker, which vibrates the column to facilitate particle sorting. Other classifications, such as sieves measured in phi units, are also sometimes used. The sieves are stacked in descending order, with the coarsest mesh at the top. The dry sediment is poured into the top of the column, and a watertight base is used at the bottom to collect the fines. The column is then carefully placed on a sieve shaker, which vibrates the sieves at a specified frequency for a set duration (typically 10 minutes). This process sorts the sediment by grain size. Each fraction is carefully weighted. Special attention should be given to removing any remaining grains from the sieve.

It is essential that the sieves in the column remain matched and not interchanged. Sieve wear ribbon must be uniform, and for this reason, when replacing sieves, the entire column (or at least all the sieves) should be replaced together with the same size.

Experimental Procedure Applied to Our Samples

The sample should first be dried in oven at 40°C and quartered to obtain an appropriate amount for grain size analyses (256 g), using the Parfenoff method (Parfenoff et al., 1970). It is important to weigh the initial dry bulk sample. The next step involves dry sieving, using a column of sieves in steel (1 phi interval), prepared in descending order of mesh size: starting from 8 mm, followed by 4 mm, 2mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, 0.063 mm, 0.032 mm, and a final pan to collect particles smaller than 0.032 mm (Fig 2.5). This setup corresponds to the Φ scale ranging from +5 to -3. Once the sieve stack is prepared, the entire sample is poured into the top sieve. The sieves are then placed onto a vibratory sieve shaker (Fig 2.5). The recommended settings for the shaker are an amplitude of 80/100, a duration of 10 minutes, and a vibrational index of 0.3 (visual scale). This ensures effective separation of particles based on size.

After completing the dry sieving, the procedure moves to the wet sieving of the same fractions. This begins with the 8 mm sieve, where the material retained is washed using tap water. The water and sediments passing the net, are collected in a 5l beaker, and poured to wash the material in the next sieve. This process is repeated for all sieves, ensuring that the material from each sieve is handled separately and that water flows sequentially from one sieve to the next. Each sieve's retained material is carefully transferred to a filter paper, and the specific sieve size is labelled on each filter paper. Finally, all the filter papers with their respective materials are left to dry completely in an oven over night (40°C). These dried samples can then be further analysed or stored as needed. This method allows for an accurate separation and classification of granular materials across a range of particle sizes.

2.2.4 Chemical analysis by X-ray fluorescence spectrometry (XRF)

After all fractions were dried, the next step was to prepare the selected fractions for geochemical analysis. The samples were prepared as pressed pellets mixed with a few drops of polyvinyl alcohol, which acts as a binder and does not interfere with the analysis. The prepared mixture was placed into an aluminium cup and pressed at a pressure of 15,000 kg/cm² for one minute. At the end of the process, the obtained pellet was placed in a desiccator at room temperature for 24 hours to remove the moisture introduced by the polyvinyl alcohol.



Figure 2.5 The figure illustrates the sequential steps involved in determining the grain size distribution of the sand sample. Following oven drying, a representative sample was accurately weighed and prepared for analysis (first row). The second row shows the arrangement of a standard sieve stack in descending mesh size. The third row presents the individual sieves after sieving, each containing the fraction of particles retained according to size.

The content of volatile elements present in the sample was determined by measuring the weight difference before and after calcination of 0.5 g of sample. The spectrometer used, Panalytical Epsilon 3XL, is equipped with a metal-ceramic X-ray tube with a thin window (50 μm), a rhodium anode, and a maximum power of up to 9 W. The voltage is programmable from 4 to 50 kV in 0.01 kV steps, while the current is programmable from 1 to 1000 μA in 1 μA steps. The spectrometer chamber can be maintained under a helium atmosphere when analysing light elements or in air for heavier elements. Inside, it is equipped with the following filters, which are selected depending on the element of interest: open (no filter), Cu 300 μm , Al 50 μm , Al 200 μm , Ti 7 μm , and Ag 100 μm . The sample holder is an automatic 10-position tray with a spinning mechanism. All emission lines of the elements present in the sample are simultaneously counted by a multichannel analyzer (MCA) with 4096 channels. The detector is a silicon semiconductor of the “drift chamber” type, with dual-stage Peltier cooling and an ultra-thin beryllium window (8 μm). The measured energy range is between 0.9 and 30 keV, with a resolution of 135 eV at 5.9 keV / 1000 cps. The maximum count rate per element is 200,000 cps.

The collected data were analysed using Epsilon 3 software with the Omnian – standardless model, which allows both qualitative and quantitative analysis (through mathematical algorithms) of unknown materials without the need for calibration curves based on standards with a matrix similar to that of the samples under analysis. The analysis was repeated under six different instrumental conditions in order to investigate the entire energy range covered by all elements and to optimize the quantitative determination of the elements of interest.

The instrumental conditions applied for element determination were as follows:

Table 2.1 Instrumental conditions used for X-ray fluorescence (XRF) analysis.

Conditions	kV	Filter	Atm	Measurement Time	Range
Omnian	50	Ag	Air	60	Primary Radiations
Omnian 1	50	Cu-300	Air	180	K α con Z > As
Omnian 2	20	Al-200	Air	120	K α con Z > Cr e Z < Ge L con Z > Re e Z < U
Omnian 3	12	Al-50	Air	180	K α con Z > K e Z < V L con Z > Sb e Z < W
Omnian 4	9	Ti	Helium	300	K α con Z > Cl e Z < Ar
Omnian 5	5	None	Helium	300	K α con Z > Na e Z < S

RESULTS AND DISCUSSION

3. GRANULOMETRIC ANALYSIS AND GEOCHEMICAL ANALYSIS

3.1 Introduction

The sand and sandstone deposits are widely distributed across Italy and Europe, but only small deposits are eligible for potential source of glass production. Sands having the correct specification for specific type of uses (such as flat glass, container glass) are very restricted as the deposits that contain them are often heterogeneous and varied. Therefore, all sand resources may require certain processing steps to achieve the proper form for use. Moreover, not all grain sizes in quartz-rich silica sand are suitable; typically, only a narrow grain-size distribution possesses the desired properties for specific glass production. Typically ranging in 0.5-0.125mm is considered best grain size for less impurities and contaminants depending on the sand quality (Bide et al., 2020; Fornelli & Micheletti, 2021b). So, granulometric analysis of sand determines the distribution of particle sizes within a sample using methods like sieving. The process involves separating the sand into different size fractions, weighing each fraction, and calculating the percentage of each size which can be used to assess properties like strength, workability, or suitability for construction and geological studies. In glass industry granulometric analysis is run to estimate the purest grain size with minimal impurities contained. In this chapter, by using granulometric analysis, the geochemistry of different grain size is analysed from single sample. The procedure for the granulometric analysis was explained in detailed in Chapter 02.

Two samples, S1 and S2, were received for granulometric analysis to assess their respective grain-size distributions along with analysis of the purity of quartz in specific grain size. Sample S1 corresponds to the feed material entering the wet cleaning process, whereas Sample S2 represents the material collected downstream of the fourth grinding stage in the glass production line. So, first the samples were dried in oven at 40°C and quartered to obtain an appropriate amount for grain size analyses, using the Parfenoff method (Parfenoff et al., 1970). It is important to weigh the initial dry bulk sample. The next step involves dry sieving, using a column of sieves in steel (1 phi interval), prepared in descending order of mesh size: starting from 8 mm, followed by 4 mm, 2mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, 0.063 mm, 0.032 mm, and a final pan to collect particles smaller than 0.032 mm. This setup corresponds to the Φ scale ranging from +5 to -3. Once the sieve stack is prepared, the entire sample is poured into the top sieve. The sieves are then placed onto a vibratory sieve shaker (Fig 2.5). The

recommended settings for the shaker are an amplitude of 80/100, a duration of 10 minutes, and a vibrational index of 0.3 (visual scale). This ensures effective separation of particles based on size. After completing the dry sieving, the procedure moves to the wet sieving of the same fractions. This begins with the 8 mm sieve, where the material retained is washed using tap water. The water and sediments passing the net, are collected in a 5l beaker, and poured to wash the material in the next sieve. This process is repeated for all sieves, ensuring that the material from each sieve is handled separately and that water flows sequentially from one sieve to the next. Each sieve's retained material is carefully transferred to a filter paper, and the specific sieve size is labelled on each filter paper. Finally, all the filter papers with their respective materials are left to dry completely in an oven over night (40°C). These dried samples can then be further analysed or stored as needed. This method allows for an accurate separation and classification of granular materials across a range of particle sizes.

The granulometric analysis of dry and wet sieving are presented below. For sample S1, the results show that both methods yield similar percentages for coarser fractions, indicating minimal difference in larger particle retention. However, as the particle size decreases, a noticeable divergence appears, applying our method with sieves of 22 cm in diameter. Dry sieving tends to retain a higher percentage in the mid-size ranges (1 mm to 0.25 mm), possibly due to particle aggregation or incomplete passage through the sieves. In contrast, wet sieving proves more effective for finer particles, especially below 0.125 mm, with significantly higher retention at 0.032 mm and <0.032 mm. This trend reflects the improved disaggregation and mobility of fine particles when water is used, highlighting wet sieving as a more reliable method for analysing finer soil or sediment fractions. The granulometric analysis results for sample S2, obtained through both dry and wet sieving methods, indicate minimal variation between both sieving. This consistency suggests that the sample is clean as compared to sample S1. Both sieving methods showed zero retention for particle sizes greater than 4 mm and negligible retention above 2 mm, indicating a lack of coarse material in the sample. The particle size range between 0.125 mm and 1 mm exhibited the highest retention, with both methods recording greater than 20% for each sieve fraction in this range. This suggests that the bulk of the material falls within the medium sand classification. For particle sizes below 0.125 mm, the retention percentages in both methods remained consistently low, with only marginal differences observed between dry and wet sieving (Fig 3.1 and 3.2).

Table 3.1 Grain size distribution of sample S1 recorded in weight percentage, showing the initially noted total sample weight, followed by the results of dry sieving and wet sieving analyses presented as weight percentages.

Sample: S1				
Initial dry bulk weight after micro-splitting: 255.86g				
Dry sieving			Wet sieving	
Sieve (mm)	Weight (g)	Weight %	Weight(g)	Weight %
>8	1.993	0.78	1.993	0.78
4-8	57.415	22.44	57.117	22.32
2-4	48.485	18.95	47.963	18.75
1-2	37.726	14.74	36.188	14.14
0.5-1	32.561	12.73	27.376	10.70
0.25-0.5	18.677	7.30	12.077	4.72
0.125-0.25	16.685	6.52	8.660	3.38
0.063-0.125	13.879	5.42	12.579	4.92
0.032-0.063	17.225	6.73	21.841	8.54
<0.032	8.910	3.48	12.618	4.93

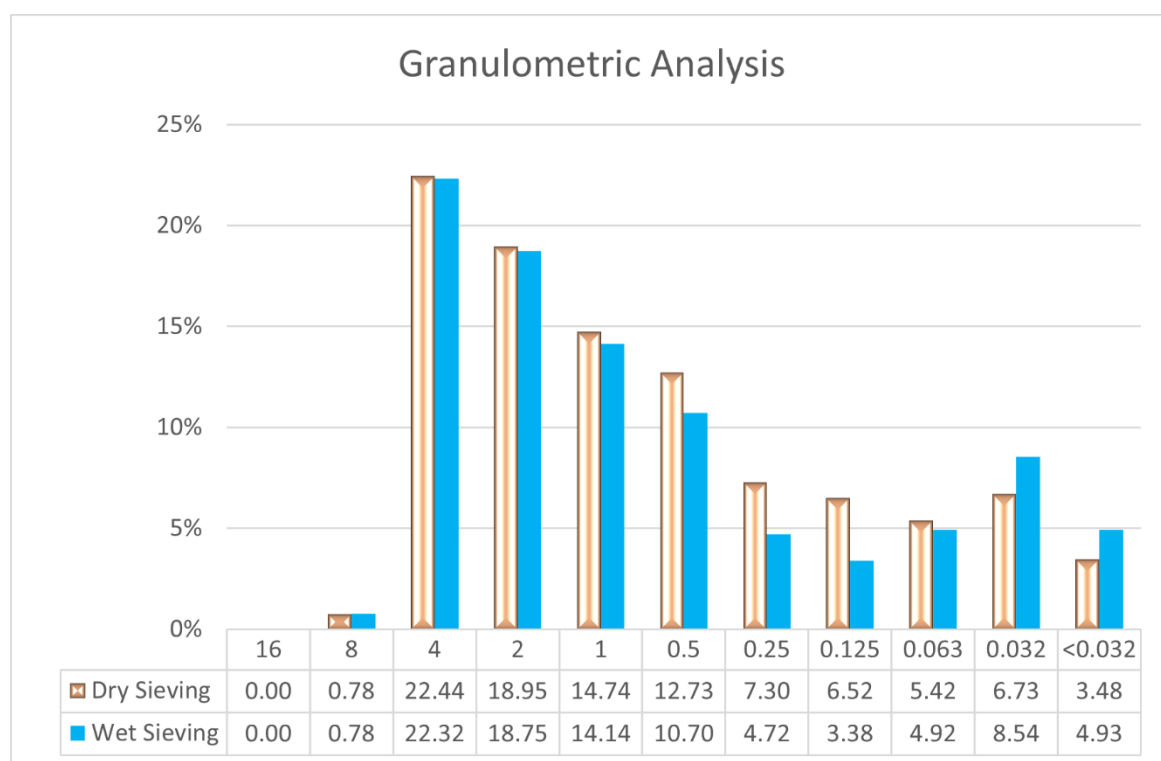


Figure 3.1 Graphical representation of the grain size distribution of Sample S1, comparing results obtained from dry sieving and wet sieving methods, expressed in weight percentage across the analysed grain size fractions.

Table 3.2 Grain size distribution of Sample S2 expressed in weight percentage, including the initially recorded total sample weight, followed by the results of dry sieving and wet sieving analyses presented as weight percentages.

Sample: S2				
Initial dry bulk weight after micro-splitting: 249.004g				
Dry sieving			Wet sieving	
Sieve (mm)	Weight (g)	Weight %	Weight(g)	Weight %
>8	0	0	0	0
4-8	0	0	0	0
2-4	0.015	0.01	0.015	0.01
1-2	0.330	0.13	0.226	0.09
0.5-1	73.391	29.47	73.951	29.70
0.25-0.5	88.632	35.59	88.923	35.71
0.125-0.25	53.165	21.35	53.005	21.29
0.063-0.125	24.410	9.80	24.476	9.83
0.032-0.063	7.068	2.84	7.217	2.90
<0.032	1.447	0.58	1.731	0.70

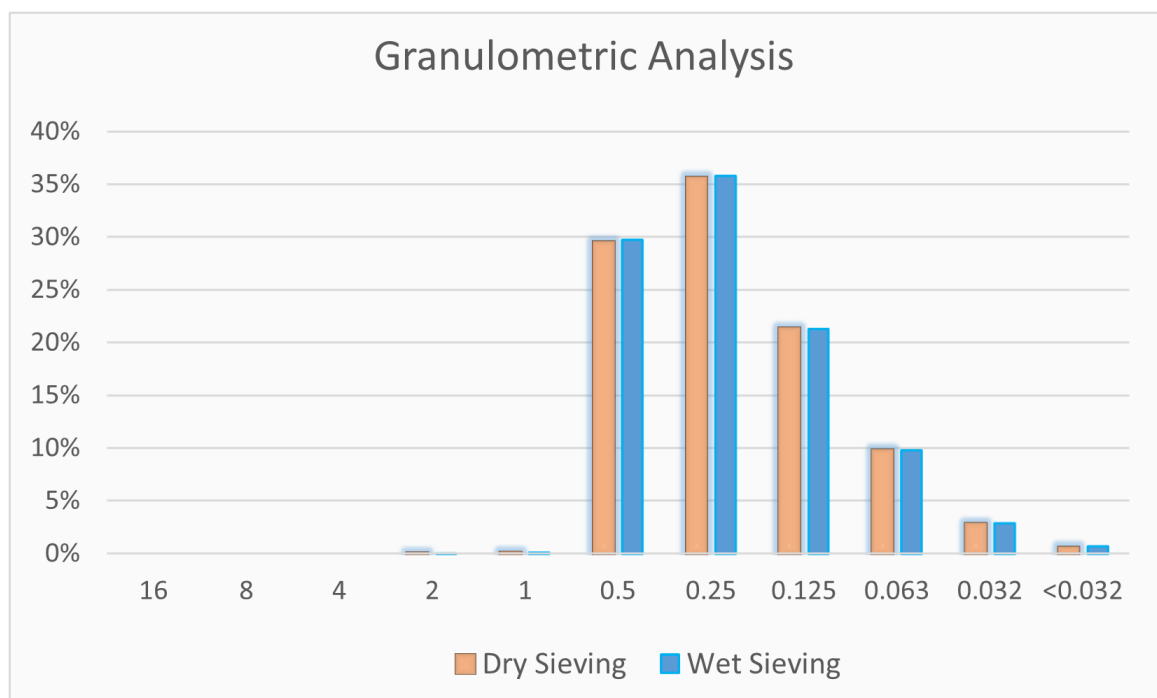


Figure 3.2 Graphical representation of the grain size distribution of Sample S2, comparing results obtained from dry sieving and wet sieving methods, expressed in weight percentage across the analysed grain size fractions.

3.2 Geochemistry of individual grain size (XRF)

The grain-size fraction between 0.032 and 1 mm was selected for X-ray fluorescence from both samples to enable a consistent comparison and to check the quartz purity. As sample S1 represents the feed material to the wet cleaning process, and sample S2 corresponds to the material obtained downstream of the fourth grinding stage. After the wet cleaning procedure and subsequent grinding, the grain-size distribution shifts toward finer particles. This is evident from the weight percentages in Sample S2 (Table 3.2), where a higher weight percentage of material is concentrated in the finer fraction compared to S1, indicating the progressive reduction in particle size caused by the treatment processes.

XRF analysis indicates that, in Sample S1, fractions A (32–63 μm), B (63–125 μm), and C (125–250 μm) account for approximately 8.54 wt%, 4.92 wt%, and 3.38 wt%, respectively. These fractions contain ~93 wt% SiO_2 , with Al_2O_3 ranging from 3.55 to 3.84 wt%, Fe_2O_3 from 0.58 to 0.64 wt%, and TiO_2 from 0.06 to 0.08 wt%. For the coarser fractions D (250–500 μm) and E (500–1000 μm), SiO_2 content in Sample S1 increases to 94–95 wt%, accompanied by a decrease in impurity oxides (TiO_2 : 0.05–0.06 wt%, Fe_2O_3 : 0.49–0.56 wt%, Al_2O_3 : 2.89–3.40 wt%). In Sample S2, the same fractions show further enrichment in SiO_2 (96–97 wt%) and lower impurity levels, with TiO_2 around 0.03 wt%, Fe_2O_3 ranging from 0.33 to 0.34 wt%, and Al_2O_3 between 1.77 and 1.82 wt%.

Table 3.3 XRF analysis of the selected grain size fraction from sample S1 and S2 including the weight percentage of each selected fraction. For comparison each fraction is labeled a name from A to E.

Sample	S1					S2				
Weight %	8.54	4.92	3.38	4.72	10.70	2.90	9.83	21.29	35.71	29.70
Grain Size (μm)	32-63	63-125	125-250	250-500	500-1000	32-63	63-125	125-250	250-500	500-1000
Fraction	A	B	C	D	E	A	B	C	D	E
MgO	0,13	0,14	0,12	0,10	0,10	0,01	0,01	0,02	0,04	0,04
Al_2O_3	3,55	3,84	3,59	3,40	2,89	1,19	1,05	1,50	1,82	1,77
SiO_2	93,80	93,76	93,93	94,27	95,19	97,72	98,16	97,46	96,92	97,07
K_2O	1,02	0,85	0,99	0,92	0,81	0,29	0,23	0,37	0,47	0,44
CaO	0,03	0,03	0,03	0,02	0,02	<0,01	<0,01	<0,01	<0,01	<0,01
TiO_2	0,06	0,07	0,08	0,06	0,05	0,04	0,03	0,03	0,03	0,03
Cr_2O_3	0,02	0,02	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Fe_2O_3	0,64	0,58	0,61	0,56	0,49	0,31	0,20	0,29	0,33	0,34
ZnO	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
SrO	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
ZrO_2	0,01	0,01	<0,01	<0,01	<0,01	0,02	0,01	<0,01	<0,01	<0,01
SnO_2	0,03	0,03	0,03	0,03	0,03	0,02	0,02	0,03	0,03	0,03
LOI	0,71	0,66	0,60	0,62	0,39	0,36	0,27	0,27	0,32	0,26

Notably, the fraction B (63–125 μm) in S2 contains approximately 98 wt% SiO_2 , along with significantly reduced concentrations of impurity oxides such as TiO_2 and Fe_2O_3 . This fact highlights as the most suitable size range for high-quality glass production. Also, a comparison between S1 and S2 demonstrates a consistent decrease in these impurity oxides. Overall, these changes clearly demonstrate the efficiency of the industrial treatment process in producing high-purity quartz suitable for glass manufacturing.

A comparison of the geochemical data with established compositional standards reported in the literature and adopted by the glass industry (Table 3.4) provides important insights into the industrial suitability of the investigated granulometric fractions. Based on the selected granulometric fractions, Sample S2 demonstrates a clear improvement in chemical quality relative to these standards.

In particular, fraction B (63–125 μm) of Sample S2 is identified as the most suitable for the production of colourless container glass, owing to its high SiO_2 content and very low concentrations of oxides elements, especially Fe_2O_3 and TiO_2 . These characteristics meet the stringent purity requirements necessary to minimize coloration in glass products.

Table 3.4 General specifications of the chemical composition of glass sand, outlining standard chemical requirements for the use of sands in the production of different types of glass. (modified after Fornelli & Micheletti, (2021); Khan et al. (2018); Edem et al (2014); GWP Consultants LLP, (2010).

Grade of glass	$\text{SiO}_2\%$	$\text{Fe}_2\text{O}_3\%$	$\text{TiO}_2\%$	$\text{Al}_2\text{O}_3\%$
Optical and ophthalmic	99.7	0.013	0	0.2
Tableware and lead crystal	99.6 (± 0.1)	0.01	0	0.2 (± 0.1)
Borosilicate glass	99.6 (± 0.1)	0.01	0.012	0.2 (± 0.1)
Colourless container (flint)	98.8 (± 0.2)	0.03 (± 0.003)	0.1	0.5 (± 0.1)
Clear flat glass	99.0 (± 0.2)	0.1 (± 0.005)	0.1	0.5 (± 0.15)
Insulating fibres	94.5 (± 0.5)	0.3 (± 0.05)	0.1	3.0 (± 0.5)
Coloured container	97.0 (± 0.3)	0.25 (± 0.03)	0.1	4.0 (± 0.1)
Amber glass	95.0 (± 0.3)	1.0 (± 0.03)	0.1	4.0 (± 0.1)
Green glass	95.0 (± 0.3)	1.0 (± 0.03)	0.1	4.0 (± 0.1)

Fractions A (32–63 μm) and C (125–250 μm) of Sample S2 are considered suitable for coloured glass container production. This is consistent with industrial practice, where finer particles are generally preferred due to their enhanced melting behaviour and higher reactivity, which promote more efficient fusion during glassmaking. In contrast, Fraction E (500–1000 μm) of Sample S2, although chemically within acceptable limits for coloured glass production, may present limitations related to its coarser grain size. In particular, grain size $>700\mu\text{m}$ are typically

regarded by the glass industry as less suitable, as they can negatively affect melting kinetics and reduce processing efficiency. Therefore, while this fraction meets the compositional requirements, its granulometric characteristics make it less favourable compared to finer fractions for optimal industrial performance.

Overall, the analysed fractions from Sample S2 satisfy the compositional requirements for glass manufacturing and are therefore considered suitable for industrial use. These findings are particularly relevant for Verallia, the industrial facility from which the samples were collected, which specializes in the production of coloured glass containers. The results confirm that the current processing stages effectively produce raw materials that meet the quality standards required for their intended application.

CHAPTER 04

HEAVY MINERALS AS A CONTAMINANTS

4. HEAVY MINERALS AS A CONTAMINANTS

Silica is the key constituent in production of glass, responsible for its structure, and it typically originates from quartz sand. Quartz-rich sand, commonly used as a primary raw material in glass production, may contain trace amounts of heavy minerals. In this study, heavy minerals are defined as those with a density greater than 2.90 g/cm^3 , occurring either as single grains or within rock fragments (Garzanti & Andò, 2019). In the field of sedimentology, heavy minerals are widely used technique to determine the sediments provenance, reconstruction of depositional environment and to recognize paleogeography of the source area (Chmielowska & Salata, 2020; Morton & Hallsworth, 1999). Heavy mineral studies are also useful in studies of sedimentation related to tectonic uplift, as the evolution and unroofing episodes of orogenic belts are faithfully reflected in their foreland sediments. The composition and abundance of heavy mineral assemblages are primarily controlled by the mineralogical characteristics of the source region; however, during the sedimentary cycle, the original provenance signal may be modified by various post-depositional processes. From the moment the minerals are released from their host rocks, a series of processes come into effect, operating until the assemblages are extracted from the sediment for study. The significance of factors likely to affect the reliability of heavy minerals analyses and their interpretation have been discussed in many publications (Harvey Blatt, 1967; Mackie, 1923; Morton, 1985; Van Andel, 1959; Whetten, 1973). But, in this research work, the amount of heavy minerals is analysed to estimate the level and type of impurities in the quartz rich sand rather than to investigate specific geological or sedimentological features.

In this study, the analysis of heavy minerals was conducted on quartz-rich sand samples obtained from supplier companies providing raw materials to Verallia. The exact origin and locations of most samples were not disclosed due to supplier privacy policies. All sands analysed in this study were supplied as high-purity, quartz-rich materials. In fact, the presence of heavy minerals may compromise the quality of raw material and decrease the purity factor. In the glass industry it is believed that this trace amount of heavy mineral content may also act as contaminant and impurity which may affect the coloration of transparent glass.

To determine the heavy mineral content a gravimetric separation technique is used (Andò, 2020). From the bulk samples, approximately 30g of sediment was used for wet sieving to obtain a grain size window of $15\text{-}500\mu\text{m}$, which is considered the most appropriate to identify the suite and amount of heavy minerals. The sieved fraction is mixed with a non-toxic heavy-

liquid sodium polytungstate, with a density of 2.90g/cm³, to separate the heavy and light minerals using a centrifuge. A representative aliquot of HM separated is mounted on a slide for microscopic analysis. The fractions of heavy mineral and light minerals mineral separated from the total used material are presented in (Table 4.1).

Table 4.1 Separation chart illustrating the distribution of particle-size fractions (>500 μ m, 15–500 μ m, and <15 μ m) expressed in grams relative to the initial weight. The chart also presents the corresponding heavy mineral percentage.

Sample		g	g LM	g HM	%HM
SBT	Initial Weight (g)	30.2200			
	>500 μ m	0.1654			
	15-500 μ m	30.0100	29.9853	0.0141	0.05%
	<15 μ m	0			
	total	30.1754			
TS-2	Initial Weight (g)	29.8847			
	>500 μ m	0.4209			
	15-500 μ m	29.3298	29.2677	0.0206	0.07%
	<15 μ m	0			
	total	29.7507			
PORT 40/45	Initial Weight (g)	30.4652			
	>500 μ m	0.4013			
	15-500 μ m	29.8659	29.8312	0.0146	0.05%
	<15 μ m	0			
	total	30.2672			
SRD-4V	Initial Weight (g)	30.6762			
	>500 μ m	0.3685			
	15-500 μ m	29.9249	29.7022	0.0106	0.03%
	<15 μ m	0.2138			
	total	30.2934			
SAB-2	Initial Weight (g)	31.4677			
	>500 μ m	14.7082			
	15-500 μ m	15.6318	15.7204	0.0071	0.04%
	<15 μ m	1.1277			

	total	31.4677			
V1	Initial Weight (g)	29.8267			
	>500µm	8.3976			
	15-500µm	20.2225	20.1349	0.0178	0.08%
	<15µm	0.7728			
	total	29.3929			
V2	Initial Weight (g)	27.7266			
	>500µm	5.9970			
	15-500µm	20.3129	20.0110	0.0017	0.008%
	<15µm	0.7848			
	total	27.0947			
S1	Initial Weight (g)	77.8448			
	>500µm	52.812			
	15-500µm	20.327	19.8285	0.0309	0.039%
	<15µm	4.1012			
	total	77.2402			
S2	Initial Weight (g)	35.3014			
	>500µm	8.922			
	15-500µm	25.835	25.5415	0.0305	0.086%
	<15µm	0.1552			
	total	34.9122			

The investigation of grain mount of heavy mineral fraction is carried out by using point counting technique to measure quantitatively the proportion and percentage of different single heavy minerals. The heavy mineral fraction also contains the presence of opaque mineral impurities, which are also considered, due to their contribution as the major contaminant. So, to study the opaque and semi-opaque minerals (Ti-Oxide and Fe-Hydroxides) within the heavy minerals, reflected light microscopy was used along with transmitted light and later confirmation of the mineral by using the Raman vibrational modes. After conducting point counting and optical analyses, the results indicate that the five samples of raw materials from different supplier companies (used by Verallia as a raw material) namely SAB-2, SBT, Port 40/45, TS-2, and SRD-4, contain heavy mineral percentages ranging from 0.03% to 0.07% (Table 4.1). The most frequently occurring heavy minerals include zircon, rutile, apatite,

tourmaline, andalusite and kyanite across all the five samples (Fig 4.1). The presence of these heavy minerals along with opaque mineral, may contribute as an impurity in the transparent glass, potentially impacting the production process. Furthermore, during the melting process, new minerals can crystallize and incorporated as defects within the final glass product.

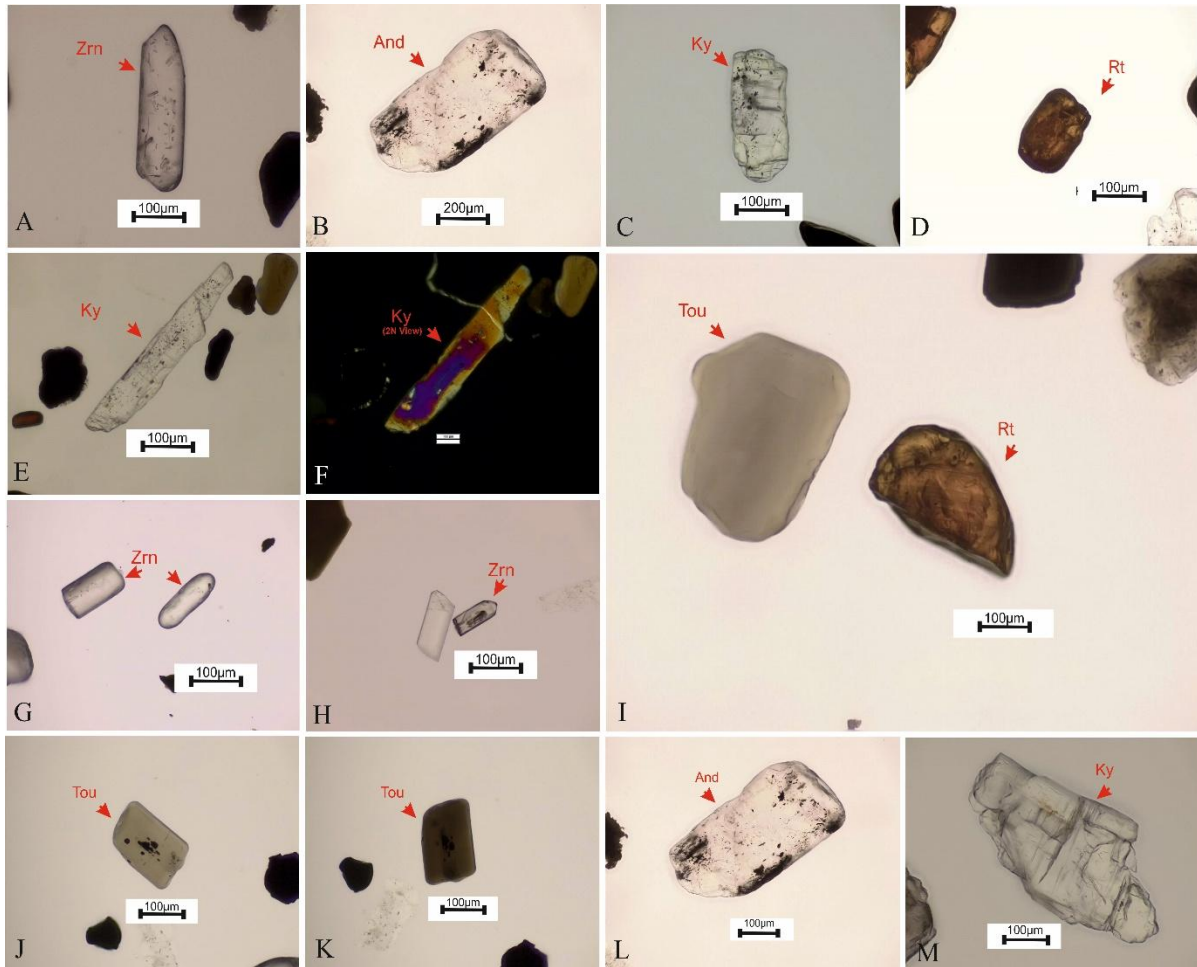


Figure 4.1 Photomicrographs of identified minerals from samples SAB-2, SBT, Port 40/45, TS-2, and SRD-4, captured using the Zed imaging tool with focus stacking. Mineral abbreviations: Zrn – Zircon, Rt – Rutile, Tur – Tourmaline, Ky – Kyanite, And – Andalusite. Labelled images: (A) Zircon, (B) Andalusite, (C) Kyanite, (D) Rutile, (E) Kyanite, (F) Kyanite in crossed polars (2N), (G) Two Zircons, (H) Zircon, (I) Tourmaline and Rutile, (J) Tourmaline, (K) Tourmaline in crossed polars (2N), (L) Andalusite, (M) Kyanite.

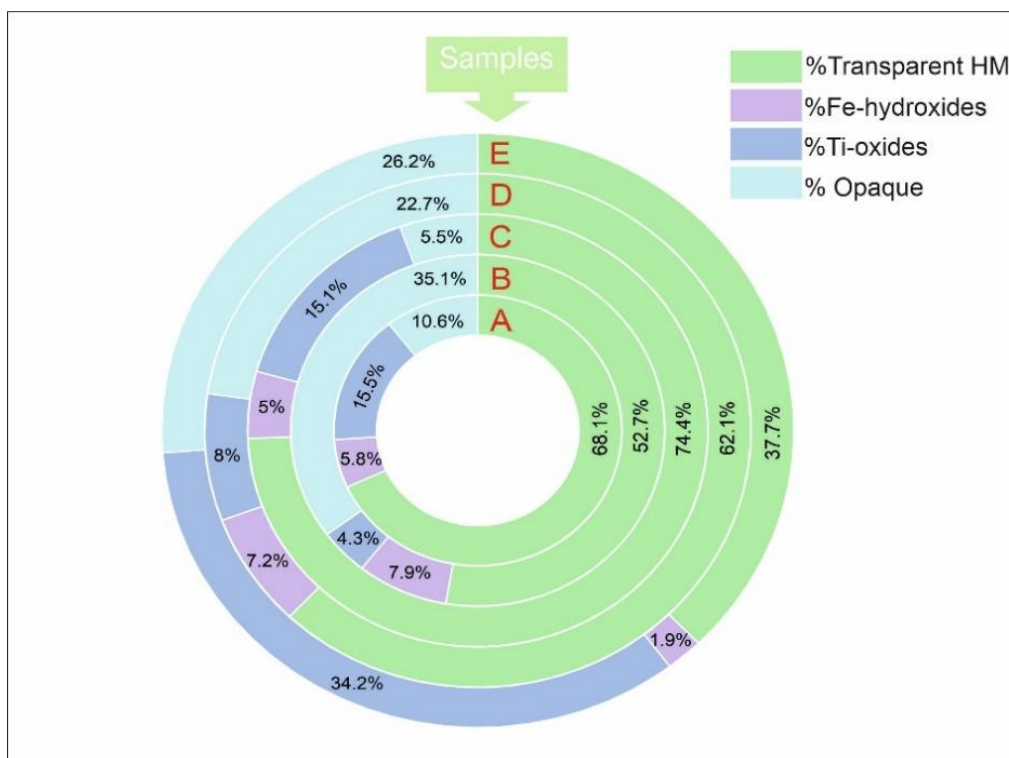


Figure 4.2 Donut chart showing the percentage distribution within the heavy mineral fraction, including transparent heavy minerals, Fe-hydroxides, Ti-oxide, and opaque minerals, illustrating their relative contributions to the total heavy mineral assemblage. (A=SBT, B=TS-2, C=Port40/45, D=SRD-4V, E=SAB-2)

Mineralogy of sample V1 and V2:

These two samples were basically not the direct raw material from the quarry, but they are collected from the recycled crushed glass cullet. These samples i.e. V1 and V2 which was collected during the cleaning procedure of raw material in the production process of glass. V1 (wet) was obtained from the wet cleaning procedure while the V2 (dried) was obtained after the wet cleaning procedure. The separation chart (Table 4.1) shows the proportion of each fraction. In sample V1, by using point counting technique the heavy mineral proportion is around 0.08%. The transparent heavy mineral recorded are Zircon, Almandine, Apatite, and Epidote. While in sample V-02 the proportion of heavy mineral is around 0.01% which is very low to make the glass mount for further optical microscopic investigation. This low heavy mineral concentration indicates the high purity the material. This is further supported by the fact that the sample was collected after the wet-cleaning process, demonstrating the effectiveness of the cleaning procedure.

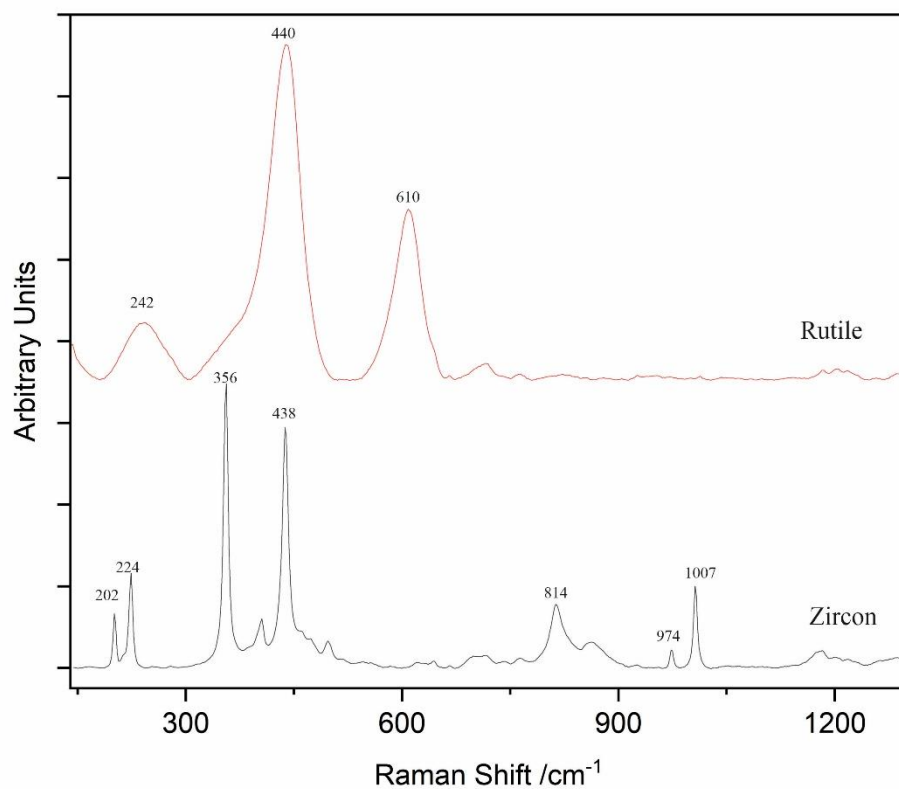


Figure 4.3 Raman spectra of recorded rutile and zircon.

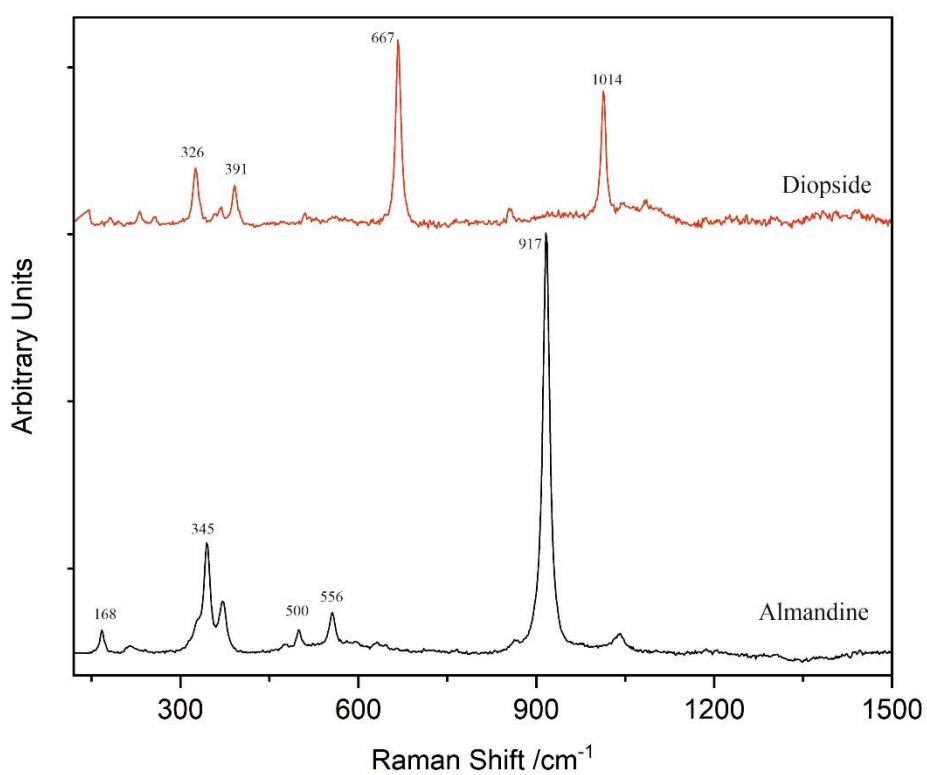


Figure 4.4 Raman spectra of recorded diopside and almandine.

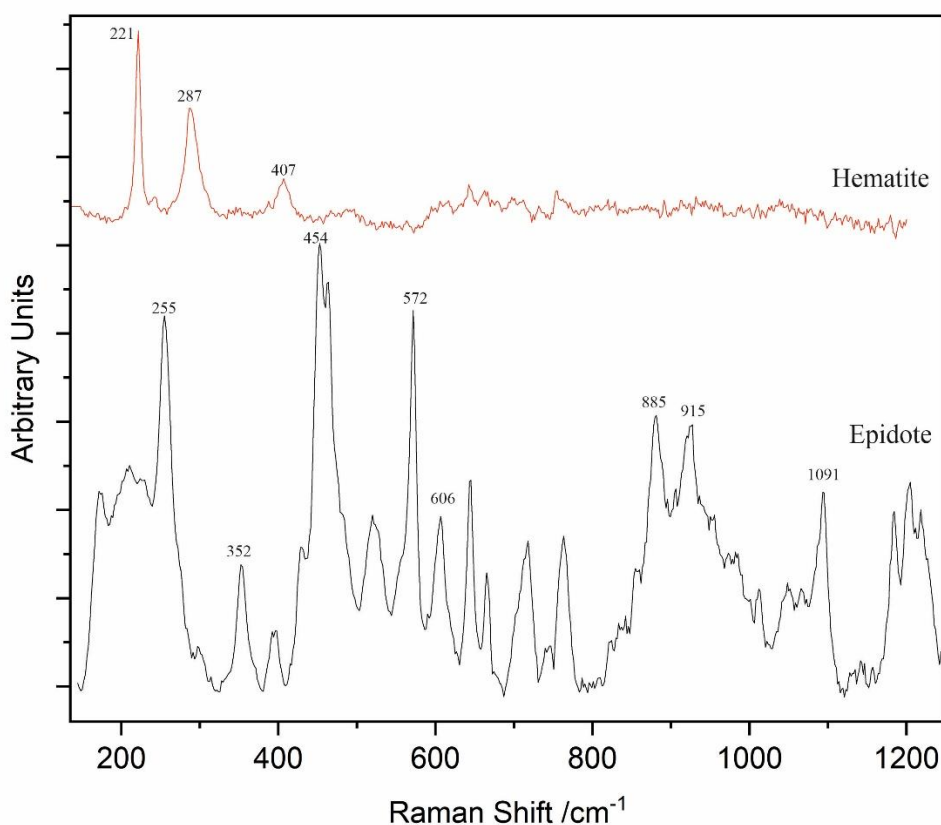


Figure 4.5 Raman spectra of Hematite and Epidote recorded from our samples.

Mineralogy of sample S1 and S2:

One of the methods to evaluate the quality of high purity quartz raw materials is by observing the structure, grain size, colour, and impurity components of hand specimens visible to the naked eye. Initially combining theory with experience, the sample S1 was separated by hand picking and using visual inspection in >8mm, 4-8 mm and 2-4 mm grain size around 3 categories was established: *clean colourless pure quartz*; *quartz with greenish colour*; *quartz with yellowish and orange-reddish colours*. We have identified main minerals in different type of fragments in these two grain sizes. The Raman spectroscopic analysis of “*clean colourless pure quartz*” fragments >8mm confirmed the presence of transparent quartz while the “*quartz with greenish colour*” fragments are composite rock fragments with dominant quartz and green variety of mica (Fig 4.6). The same procedure was applied in the 4-8mm grain size class. This class contains 22.1% of reddish or yellowish orange weathered rock fragments. The analysis indicates the presence of quartz with transparent to blueish appearance. In the same fragment the orange part was identified as goethite (Fe-hydroxide) (Fig 4.7). The quartz observed from other fragment is pale yellowish-brown. Raman scattering is very low in these fragments and

by increasing the laser power the hydroxides are easily burned, because they contain also organic molecules (C disordered bands in the spectra of these weathered rock fragment). The same procedure was applied in the 2-4mm. This class contains 8.4% of yellowish-orange weathered rock fragments. Two different fragments were analysed. The Raman spectra of first fragment indicated the presence of quartz having yellowish appearance. But the analysis of other fragment shows no signal but gives very low presence of green muscovite. The same procedure was applied in the 1-2mm grain size class. The first fragment analysed confirms as dominant the presence of quartz, while another fragment picked for the colour, it shows the presence of quartz associated with green micas very similar to muscovite (it is not chlorite).

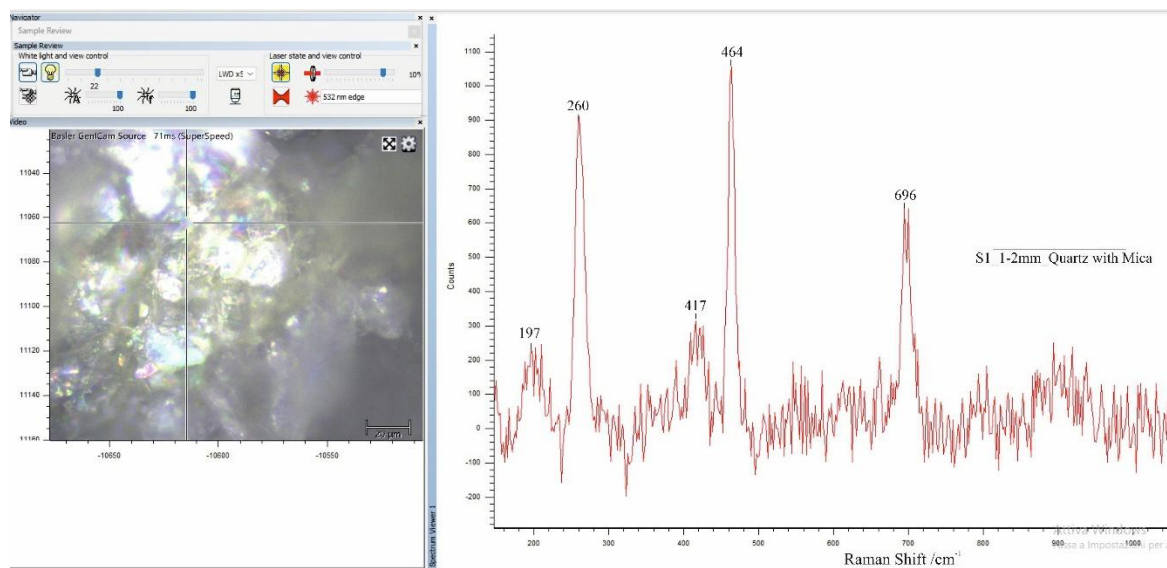


Figure 4.6 Raman spectra of quartz associated with green coloured variety of Mica from sample S1 (1-2mm).

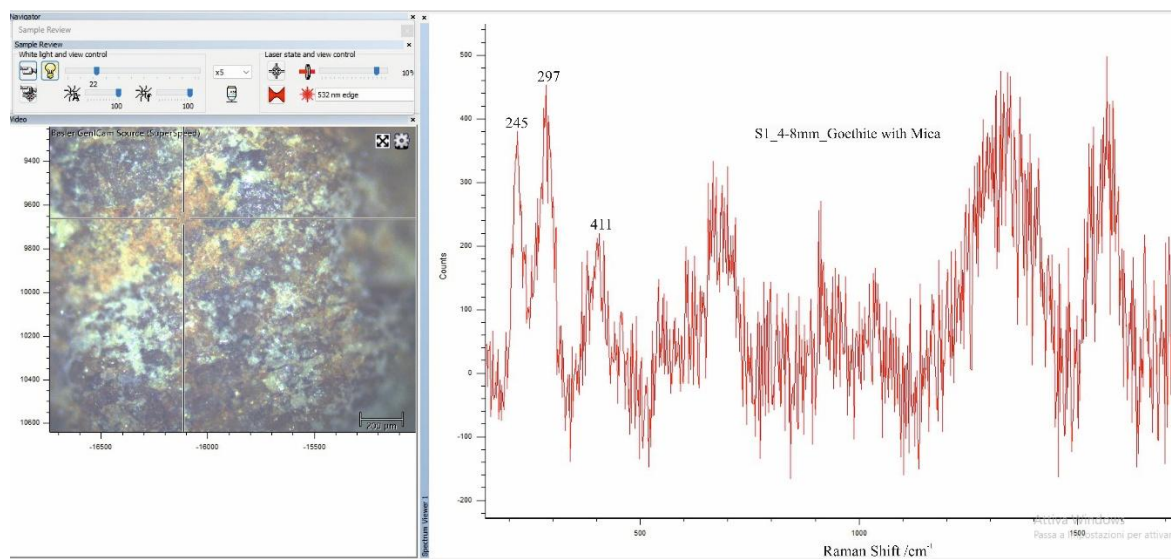


Figure 4.7 Raman spectra of Goethite associated with Mica from sample S1 (4-8mm) inset with live photo.

Similarly, from S2 the representative fragments were analysed from particle size fractions 1–2 mm, 0.5–1mm and 0.25–0.5mm. In fraction 1–2 mm, two distinct fragments were analysed. The Raman spectrum of the first fragment, exhibiting a pinkish colour, confirmed the presence of quartz. The second fragment revealed quartz associated with a green variety of mica, as indicated by its spectral features. Similar procedures were applied to fraction 0.5–1 mm and Raman spectroscopy of selected fragments confirmed the presence of quartz. In addition, reddish-orange spots as shown in fig 4.7, ranging from a few microns to approximately 10µm in size, were identified. The Raman spectra of these spots indicated the presence of goethite. The fraction 0.25–0.5 mm primarily consisted of transparent and white grains, with few green and reddish-coloured particles. Raman analysis of a representative reddish grain (approximately 400µm in size) confirmed the presence of quartz along with Fe-hydroxide. Therefore, after this hand specimen investigation the sample S1 and S2 was quantitatively analysed using the gravimetric separation technique for determining nature and content of heavy mineral (shown in table 4.1). Sample S1 represents the raw quarry material and exhibits a heterogeneous grain-size distribution, ranging from silt-size particles to pebbles. This sample material was collected after undergoing standard industrial comminution stages, including primary (jaw crusher), secondary (cone crusher), and tertiary (cone crusher) crushing. Following gravimetric separation, the overall proportion of heavy minerals in sample S1 was approximately 0.039%. Within this heavy mineral fraction, the concentration of Ti-oxide and Fe-hydroxide is 8.19% and 4.26%, respectively shown in Fig 4.9.

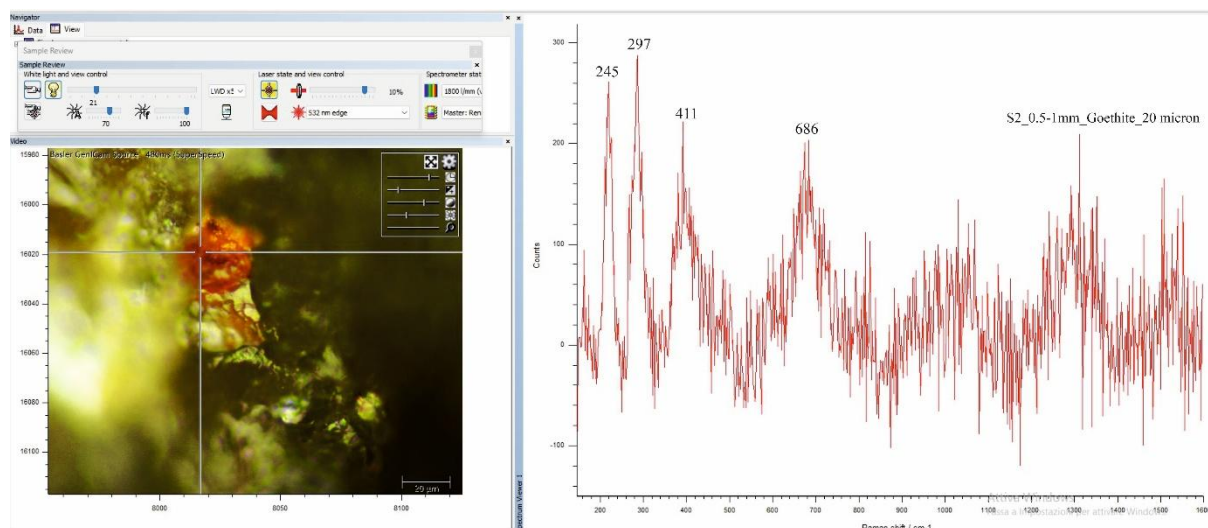


Figure 4.8 Raman spectra of goethite, showing characteristic peaks inset with live photo.

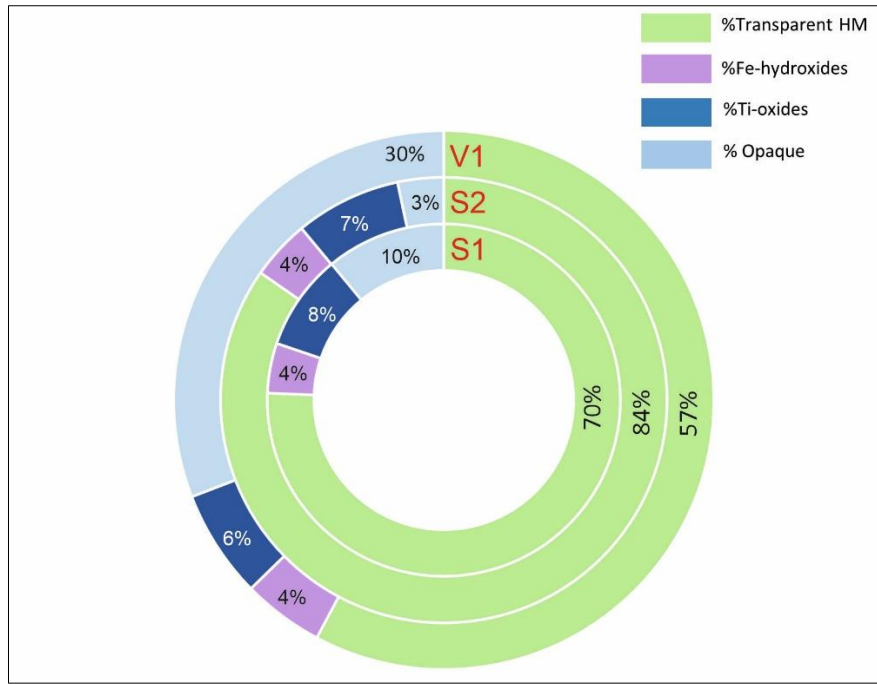


Figure 4.9 Donut chart representing the percentage distribution within the heavy mineral fraction, including transparent heavy minerals, Fe-hydroxide, Ti-oxide, and opaque minerals, illustrating their relative contributions to the total heavy mineral assemblage.

Through optical investigation and confirmation with Raman vibrational mode the recorded heavy minerals are muscovite, zircon and rutile as shown in Fig 4.10. Sample S2, in contrast, consists of material collected after the complete wet cleaning process. In comparison, sample S2 exhibited a higher heavy mineral fraction of approximately 0.086%, indicating a greater concentration of heavy minerals than in S1. The corresponding proportions of Ti-oxide and Fe-hydroxide within the heavy mineral fraction of S2 were 7.66% and 4.33%, respectively shown in (Fig 4.9). The measured heavy mineral concentration for S2 was notably higher than that of S1. This suggests that either the contamination of sample S2 at some stages or the significant proportion of heavy minerals resided in the 15-500 μ m fraction, and that the wet processing step enhanced the resultant heavy mineral concentration within the 15–500 μ m size range.

Discussion

The concentration of heavy mineral in silica sand is a critical parameter controlling the quality of glass produced. Even a slight increase in heavy mineral amount along with Fe, Ti content can impact the quality and coloration of final glass product. A slight increase in Fe content can impact the undesirable coloration typically green, yellow, or red. Therefore, it is believed that

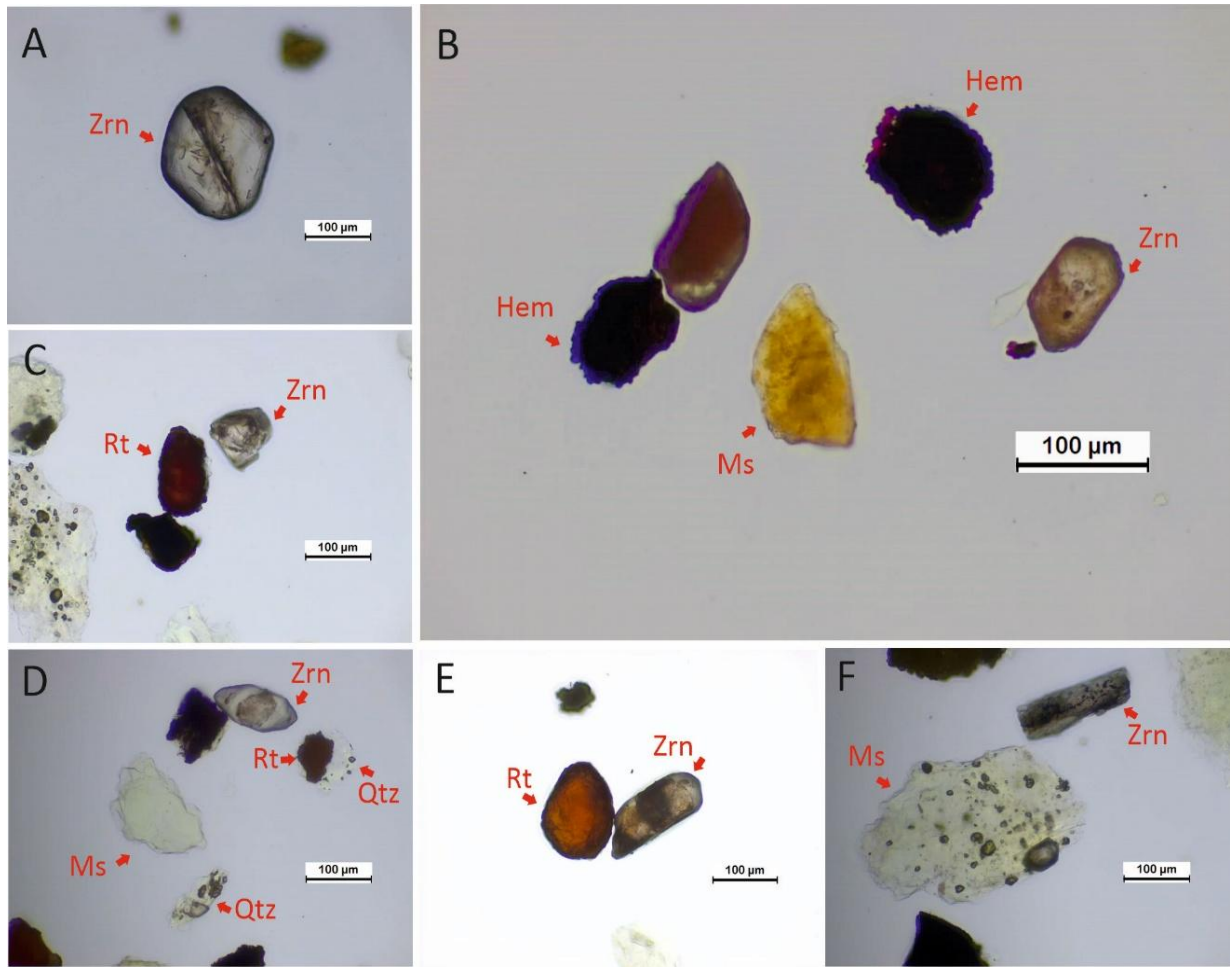


Figure 4.10 Photomicrographs of identified minerals from samples S1 and S2, captured using the Zed imaging tool with focus stacking. Mineral abbreviations: Zrn – Zircon, Rt – Rutile, Ms–Muscovite, Hem–Hematite, Qtz– Quartz.

the concentration of Fe should be below 0.05% to mitigate the coloration effect in glass. This coloration can be partially mitigated through the addition of manganese, which counteracts the iron-induced tint and may produce a faint purple hue (Host, 1991; Goldman, 1994; Heck, 2002). The presence of heavy minerals as impurities within the quartz-rich sand used as a raw material for glass production. In the namely SAB-2, SBT, Port 40/45, TS-2, and SRD-4, the proportion of heavy minerals, illustrated in the Fig 4.2, ranges from 0.02 to 0.07%. Although these values appear low, but their impact is significant because the presence of oxides along heavy minerals.

In particular, the measured proportions of Ti-oxides and Fe-hydroxides in these samples are not negligible with respect to the requirements for producing transparent glass. Even small concentrations of these phases can impart undesirable coloration or reduce optical clarity which was also observed in the final glass products. Therefore, the detected levels of Ti- and Fe-

bearing impurities indicate that further beneficiation or purification of the raw sand may be necessary to achieve the chemical purity demanded by high-quality glass manufacturing.

It is also evident that heavy mineral impurities are commonly present in the examined quartz sand samples, and their removal is achievable through appropriate cleaning procedures used in glass production. A comparison between samples V01 and V02 further demonstrates the effectiveness of such beneficiation techniques. Before the wet-cleaning process, sample V01 contained approximately 0.08% heavy minerals. In contrast, the post-cleaning results for sample V02 show a reduced concentration of about 0.008%. This represents a substantial decrease in impurity content and highlights the potential of wet-cleaning methods to significantly enhance the purity of quartz-rich sand intended for transparent glass manufacturing.

CHAPTER 05

**RAMAN SPECTROSCOPY: A NOVEL
TECHNIQUE IN GLASS INDUSTRY**

5. RAMAN SPECTROSCOPY: A NOVEL TECHNIQUE IN GLASS INDUSTRY

5.1 Introduction

In the glass industry, quantifying and identifying the impurities are crucial step in yielding excellent quality glass products. In the routine production process, there are several impurities recorded in the final glass products (bottle & jar), which needs to recognize correctly and rapidly. In many glass industry the operators are using optical microscopy to study and identify the impurity by using optical properties and comparing the physical appearance with previous reference literature. In Verallia, the operators are using the “Color Atlas of Stones in Glass” (a guidebook) for the identification of mineral impurities. By using optical properties, the encountered mineral impurities are challenging to analyse due to their altered physical properties, rendering it inaccessible to ascertain their origin and nature. So, in glass industry the new techniques are required for rapid and correct identification of mineral impurity. Therefore, Raman spectroscopy is one of the most multifaceted and user-friendly technique, acting as a pivotal addition for analysis of mineral impurities encountered in the final product in glass industry. Consequently, Raman spectroscopy could be employed to accurately identify the mineral impurity, paving the way for their effective removal based on their type and nature.



Figure 5.1 Representative image of the Renishaw Qontor Raman spectrometer used for all analyses in this study. The image is obtained from the manufacturer's website and corresponds to the same model as the instrument used in this work.

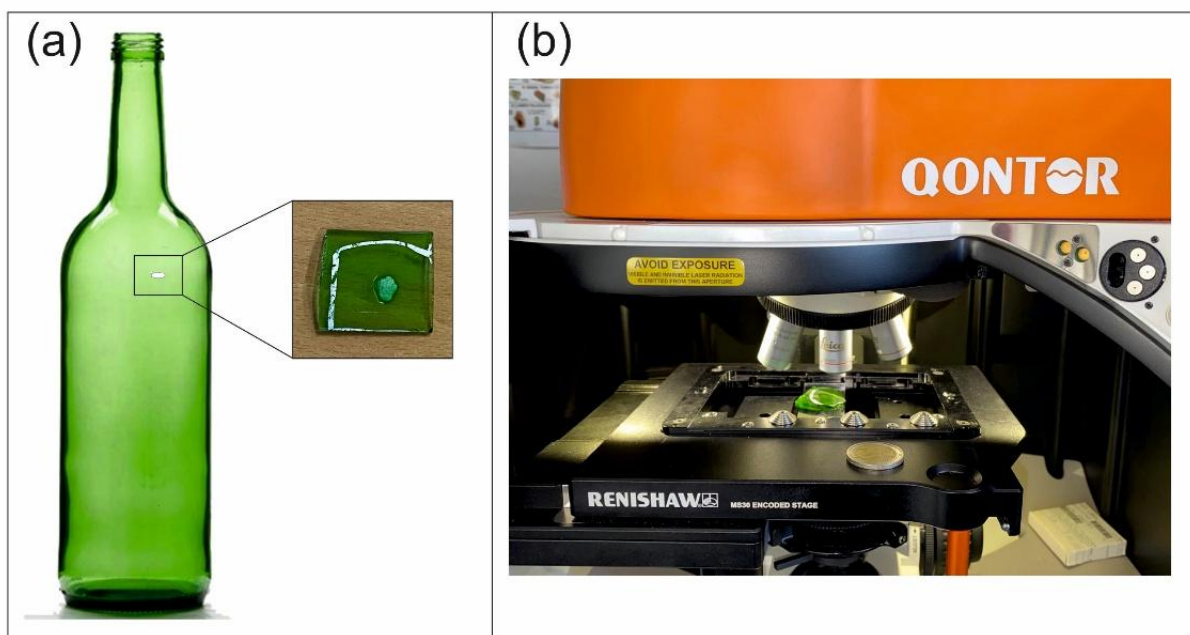


Figure 5.2 (a) Green bottle containing the impurity and the glass piece extracted from it. (b) Renishaw Qontor spectrometer, stage configuration with the glass sample ready for analysis.

This investigation improve the capability of the operator to distinguish all possible inclusions, encountered in these glasses along with more accuracy and efficiency. This, in turn, simplifies pinpointing the source of impurities with greater convenience. Thus, this technique is especially valuable for identifying mineral impurities commonly found in the glass industry.

This chapter provides an insights to the collected mineral impurities in glass cut pieces encountered in final finish of glass bottles from the industry. These analysed glass cut pieces belong to different sets. The samples labeled with series “A” (Table 5.1), were previously used as reference guide for recognizing newly recorded mineral impurity by comparising optical properites. The sample labeled with series “B” (Table 5.1) belongs to the daily recorded impurities, which were previously named by operator using the optical microscopy at Verallia. Furthermore, the sample series “C” (Table 5.2) was the glass pieces received from Verallia as part of daily recorded impurities, require more rapid and efficient identification.

In this study, the glass pieces containing the impurity were placed on the stage of Renishaw Qontor spectrometer, equipped with a Leica microscope, with objectives (2.5x, 5x, 10x, 50x long working distance and 100x) and a solid state green laser 532 nm, with autofocus in z. Before each session of analyses, we have calibrated the instrument, using an internal silicon wafer with a band at $520.5 \pm 0.3 \text{ cm}^{-1}$. The acquisition time was regulated, depending on the scattering of the inclusion and a standard setting was: 1 second, with a power of the laser from 10 to 50% and 30 accumulations. The power of the laser at the sample was $\sim 15 \text{ mW}$. The error

of each measurement is calculated as $\pm 1\text{cm}^{-1}$. Spectral manipulation was reduced to minimize the bias introduced by the operator and it was limited to a baseline adjustment, smoothing using the Renishaw Wire 5.6 software package. Assignment of Raman vibrational modes and spectra was realized by comparison with literature data and in-house database. Optical images of mineral impurities in the glass samples were captured using a Leica DM 750P optical microscope equipped with a 10x, 20x objectives, with installed camera Leica ICC50W, having a software allowing to perform a stack in zed, focusing different layers in the same inclusion and obtaining 3D images of each impurity as shown in (fig 5.3).

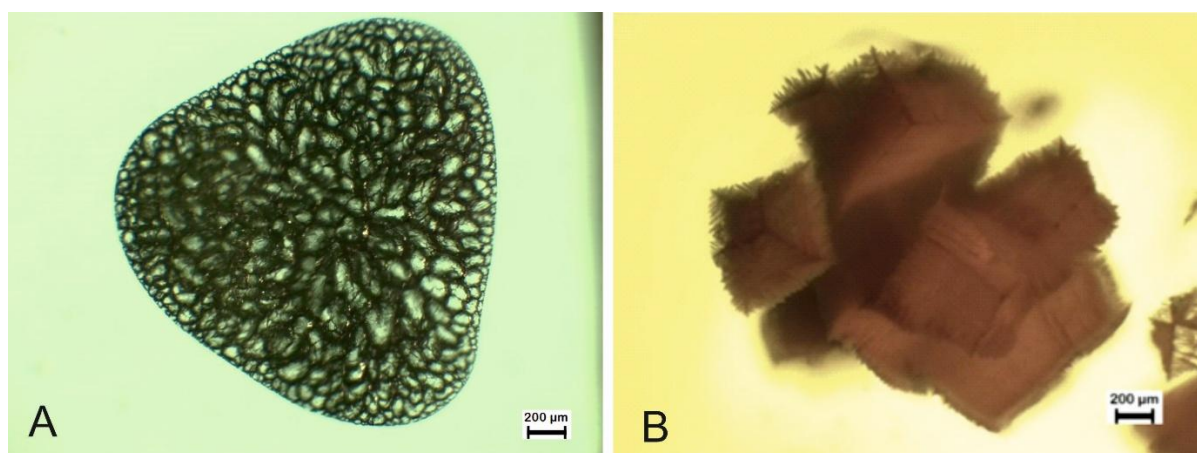


Figure 5.3 3D image of the baddeleyite and cristobalite captured using the stack in zed imaging tool of the Leica microscope.

The various Raman spectra was observed from different set of glass cut piece samples. Indeed, the identification of certain impurities previously analysed using optical microscopy has been found to differ when examined through Raman spectroscopy. The description of each recorded mineral impurity are described below across the samples in (Table 5.1 & 5.2).

Table 5.1 List of impurities recorded from glass pieces; including identification made by microscope at Verallia and identification made by Raman spectroscopy at UNIMIB.

SAMPLE # (BAG-A & B)	IDENTIFICATION BY MICROSCOPE AT VERALLIA (V)	IDENTIFICATION BY RAMAN SPECTROSCOPY AT UNIMIB (B)
A_01	Corundum	Baddeleyite
A_02	Alumina	Corundum
A_03	Carnegieite	Unknown Spectra
A_04	Sulphates	Selenium
A_05	Molybdate-Na	Molybdate
A_06	Metallic Silica	Silica
A_07	Nepheline	Cristobalite
A_08	Cristobalite	Cryolite
A_09	Baddeleyite	Baddeleyite
A_10	Quartz	Cristobalite
A_11	Corundum	Molybdenite
A_12	Cassiterite	Cassiterite
A_13	No identification	Cristobalite
A_14	Cassiterite	Cassiterite
A_15	Zirconio	Cristobalite
A_16	Silica/Quartz	Cristobalite
A_17	Corundum	Quartz
A_18	Tridimite	Unknown Spectra
A_19	Mullite	Dolomite and Calcite
A_20	Corundum	Baddeleyite
A_21	Devitrified	Wollastonite
A_22	Cromite	Cryolite
A_23	Devitrified	Unknown Spectra
B_01	Cromite	Cryolite
B_02	Ceramic	Unknown Spectra
B_03	No identification	Corundum
B_04	Alumina-Zircon-Silica (AZS)	Corundum
B_05	Alumina	Corundum
B_06	Alumina-Zircon-Silica (AZS)	Corundum
B_07	Iron	Embedded Glass
B_08	Si-metallic	Embedded Glass
B_09	Si-metallic	Embedded Glass
B_10	No identification	Embedded Glass
B_11	Iron	Embedded Glass
B_12	Alumina-Zircon-Silica (AZS)	Corundum
B_13	Si-metallic	Embedded Glass
B_14	Si-metallic	Embedded Glass
B_15	Si-metallic	Embedded Glass
B_16	Si-metallic	Rutile
B_17	Glass-Ceramic	Baddeleyite
B_21	No identification	Unknown Spectra
B_22	Cassiterite	Baddeleyite
B_23	Alumina-Zircon-Silica (AZS)	Cristobalite

Table 5.2 List of the impurities recorded from glass pieces received as part of daily impurities.

SAMPLE# (BAG-C)	IDENTIFICATION BY RAMAN SPECTROSCOPY AT UNIMIB (B)
C_1	Corundum
C_2	Unfocused/Unknown
C_3	Corundum
C_4	Corundum
C_5	Corundum
C_6	Corundum
C_8	Corundum
C_10	Corundum
C_11	Corundum
C_12	Corundum
C_13	Corundum
C_14	Corundum
C_16	Baddeleyite
C_17	Cristobalite
C_18	Corundum
C_19	Corundum
C_20	Corundum

5.2 Baddeleyite

- **Chemical Formula:** ZrO_2
- **Microscopic observation:** Baddeleyite is one of the minerals belonging to the Baddeleyite supergroup. It is primarily composed of zirconium oxide (ZrO_2), crystallizes in the monoclinic system and exhibits a range of fascinating optical properties. It appears in brownish colour and lustre varies from vitreous to dull, and its transparency ranges from transparent to translucent. Additionally, Baddeleyite displays weak to moderate pleochroism, meaning it can show different colours when viewed from different angles under polarized light. The mineral is biaxial positive, providing further insight into its internal crystal structure and light interaction capabilities.
- **Raman Observation:** Baddeleyite is confirmed from multiple glass cut pieces (shown in fig 5.4) by interpreting the Raman spectroscopic vibrational modes. The Raman examination of all these sample gives a nice spectrum, with characteristic peaks at 441, 496, 572, 621/ cm^{-1} (Fig 5.4). In sample A_01 the observed impurity is confirmed as Baddeleyite by Raman spectroscopy which is contradictory from the previous optical microscopic observation by operator i.e. Corundum. The Raman reflection of sample A_09 also confirmed that the impurity is Baddeleyite. In sample B_17 the impurity is previously recognized as Glass-Ceramic, but the Raman spectra indicated the presence of Baddeleyite. Also, the impurity in glass cut piece B_22 was optically recognized as cassiterite, but the Raman spectra indicate the presence of Baddeleyite. This confirmation is based on Raman spectra and prominent optical properties observation. Baddeleyite have very prominent numerous Raman peaks of 441, 496, 572, 621 / cm^{-1} (Chen et al., 2019) while the primary Raman peaks of corundum typically appear around 380, 416, 643/ cm^{-1} (Palanza et al., 2008).

5.3 Corundum

- **Chemical Formula:** Al_2O_3
- **Microscopic observation:** Corundum belongs to the Haematite group and is the crystalline form of Al_2O_3 . Typically, it is known due to its hardness second only to diamond. The observed grain displays grey to greenish colour having high relief. Corundum is uniaxial negative and exhibits moderate pleochroism.
- **Raman observation:** Corundum impurities observed from studied samples gives the characteristics peaks at 380 and 416 / cm^{-1} , which from the literature was confirmed as Corundum (Berezhinsky et al., 2008), also shown in (Figure 5.5). Corundum was among

the most frequently identified impurities across numerous samples. Due to their optical appearance, corundum and baddeleyite were misidentified previously during microscopic examination by operator. In sample A_02, and B_05, the impurity corundum is previously identified as alumina by the operator. Alumina, or aluminium oxide (aluminum oxide), is better known in the mineral world as corundum. Moreover, the sample B_04, B_06 and B_12 previously identified as Alumina-Zircon-Silica (a mixture), but Raman inspection confirmed that these impurities are Corundum with characteristics peaks are 379 and 418/cm⁻¹ (Berezhinsky et al., 2008), also shown in (Fig 5.5). The term Alumina-Zircon-Silica (AZS) is used in “Color Atlas of Stones in Glass” by AGR shared by Verallia. That’s why this type of impurity was previous recognized as Alumina-Zircon-Silica (AZS) but after identifying various part of impurity, we only recorded the presence of Corundum. Also, the confirmation of the grain (impurity) from samples of “C” series was checked through Raman spectroscopy. The characteristics peaks are 379 and 418 /cm⁻¹ (Berezhinsky et al., 2008), also shown in (Fig 5.5).

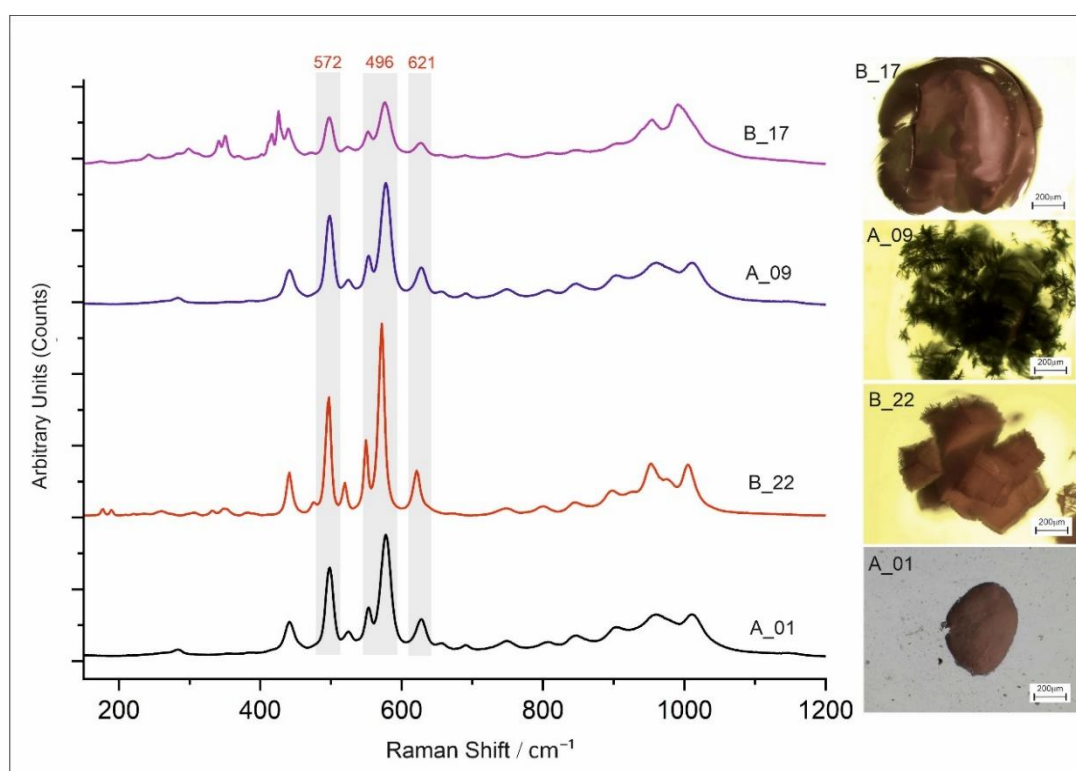


Figure 5.4 Stacked Raman Spectra of baddeleyite from studied samples. In samples, A_01 and B_22 we recognize the spectrum of baddeleyite, very similar to pure baddeleyite proposed by (Chen et al., 2019). Along with Raman spectra a corresponding set of photomicrographs of baddeleyite impurities obtained by optical microscope from different samples highlight variations in shape and optical properties

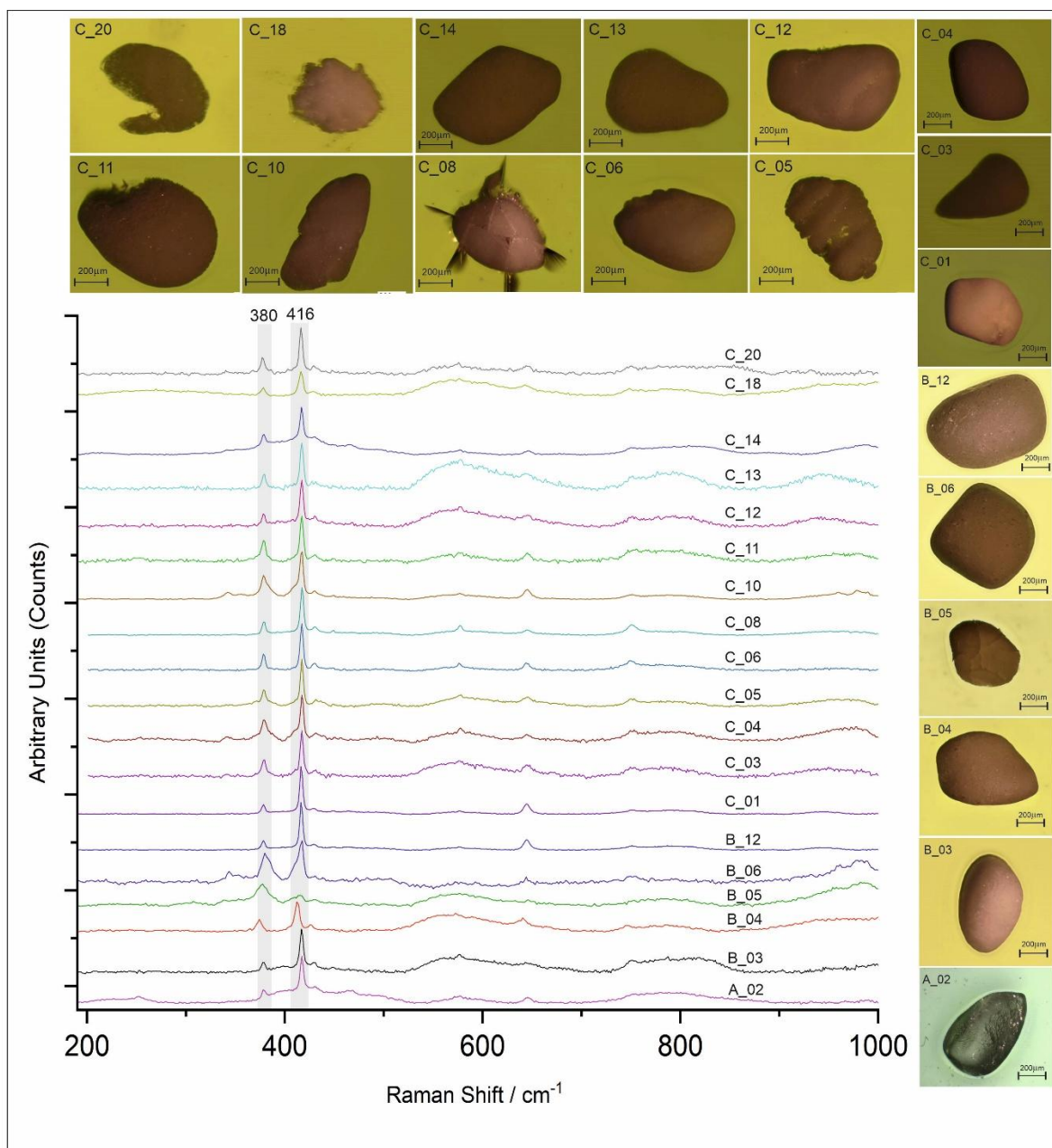


Figure 5.5 Stacked Raman spectra of all recorded corundum impurities from the analysed glass samples, alongside corresponding photomicrographs of each corundum particle. The Raman spectra show consistent peak positions, while the photomicrographs reveal varied morphological features among the corundum with a dominant subrounded shape. The colour is influenced by the green tinge of the glass and it appears as light pinkish white to pale brown.

5.4 Cristobalite

- **Chemical Formula:** SiO_2
- **Microscopic Features:** Cristobalite, a high-temperature polymorph of quartz (SiO_2), exhibits distinctive optical properties that reflect its unique crystalline structure. Cristobalite crystallizes in the tetragonal crystal system. During optical microscopic investigation, the examined crystal exhibits moderate to high relief in shades of pinkish

brown colour. Cristobalite is uniaxial positive with absent of pleochroism. The crystal surface displays glassy appearance with rounded shape.

Raman observation: Cristobalite have very prominent Raman peaks of 230, 417/ cm^{-1} (Horwell et al., 2013; Thomas, 2023). Through Raman examination in samples A_07, A_10, A_13, A_15, and A_16 the spectrum confirmed that the crystal impurity is a Cristobalite (SiO_2) (Fig 5.6). All samples give a clear Raman spectrum, with characteristic peaks at 230, 417/ cm^{-1} . In sample A_07 the recorded impurity is confirmed as Cristobalite previously identified as Nepheline. Cristobalite is pure silica (SiO_2) while nepheline is an aluminosilicate with sodium, potassium, and aluminium. The primary Raman peaks of Nepheline typically appear around 406, 487/ cm^{-1} . The Raman spectra of sample A_10 and A_16 show the presence of Cristobalite. According to optical identification, the impurity is identified as Quartz not Cristobalite. Quartz and cristobalite are both polymorphs of silicon dioxide (SiO_2), meaning they are different structural forms of the same chemical compound. Therefore, our confirmation is more based on Raman spectra as compared to optical properties observation. It is challenging to differentiate both under the microscope because both quartz and cristobalite share some similar optical properties, such as being uniaxial positive and exhibiting a vitreous lustre. However, they differ in their birefringence ranges, with quartz having a higher birefringence than cristobalite. Cristobalite have two very prominent Raman peaks of 230, 417/ cm^{-1} while the Quartz typically have a prominent peak of 465/ cm^{-1} (Trepmann et al., 2020). Also, the Raman analysis of sample A_13 shows the impurity is Cristobalite which was previously unknown by optical microscopy. Similarly, the Raman spectra of sample A_15 show the presence of cristobalite while previously it was identified as zirconia by optical microscopy. Zirconia is the artificial form of baddeleyite and is primarily composed of zirconium oxide (ZrO_2) having Raman signature peaks at 498, 573, 621/ cm^{-1} (Perevalov et al., 2020). Furthermore, in sample B_23 the Raman spectra depicts the impurity is Cristobalite while previously it is recognized as Alumina-Zircon-Silica (AZS) through optical microscopy.

5.5 Cassiterite

- **Chemical Formula:** SnO_2
- **Microscopic observation:** Optical examination indicated that the observed crystal displays high relief in pinkish colour. The crystal surface gives the homogenous appearance with few surface striations. The crystal exhibits triangular shape with rounded corners. It generally exhibits weak or no pleochroism and is uniaxial negative.

- Raman Observation:** The Raman examination from sample A_12 and A_14 confirmed that the crystal impurity is a Cassiterite (SnO_2). It gives a clear Raman spectrum, with characteristic peaks at 493, 634, 775/ cm^{-1} (Andò & Garzanti, 2014). The position of peaks is shown in (Fig 5.7). Cassiterite is one of the minerals belonging to Rutile group. Cassiterite is an oxide mineral and primarily composed of tin dioxide. Cassiterite crystallizes in the tetragonal system, often forming prismatic or bipyramidal crystals. Optically, cassiterite is uniaxial positive and shows weak to moderate pleochroism. This impurity from both samples is also confirmed as Cassiterite by optical microscopy examination.

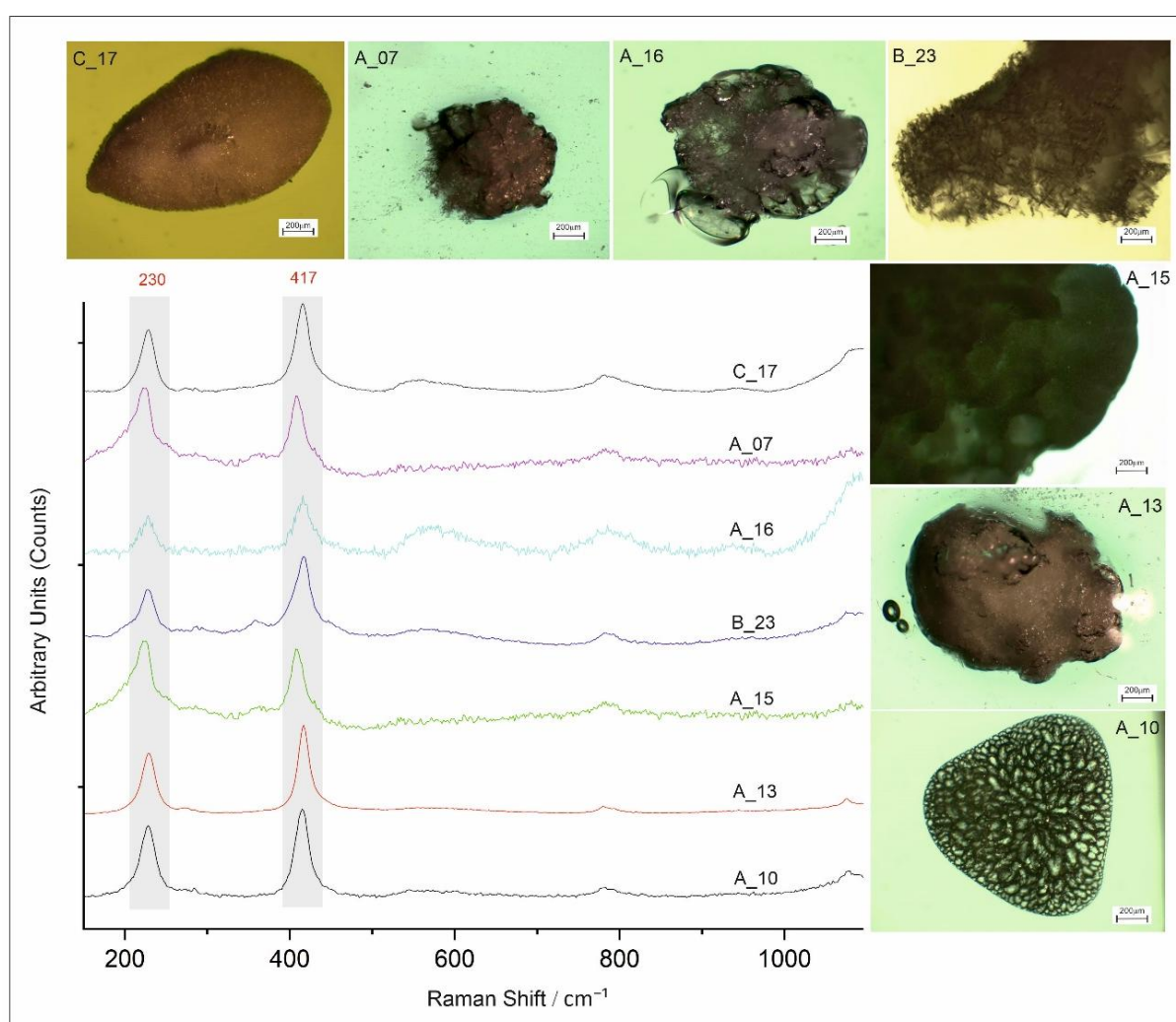


Figure 5.6 Stacked Raman spectra of cristobalite impurities from studied samples. The signature peaks (230, 417 cm^{-1}) across all the samples are identical and in good agreement with the pure cristobalite Raman spectra proposed in literature (Bates, 1972; (Bates, 1972; Swainson et al., 2003b; Horwell et al., 2013; Liu et al., 2020). Accompanying set of photomicrographs show cristobalite in different morphologies. This mineral is encountered in different shape, either subrounded or subrounded and corroded, as aggregates of needles like tiny crystals, and in sample A_10 it shows a weird texture resembling aggregates of minute lobate cells.

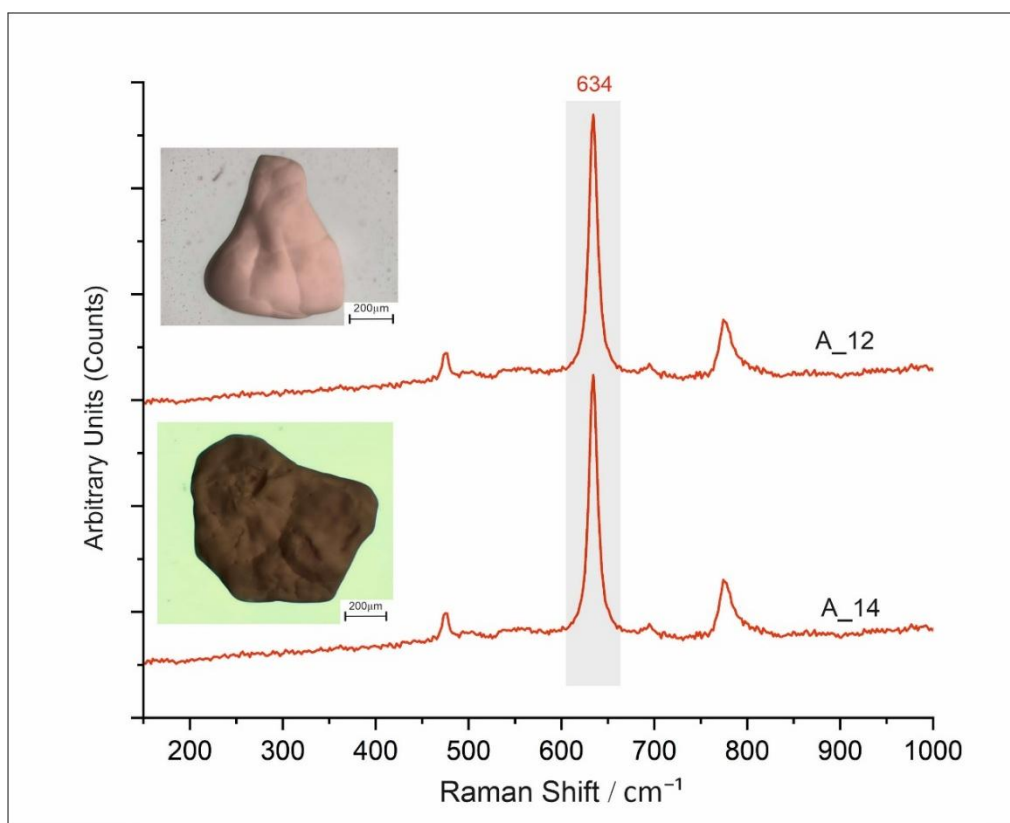


Figure 5.7 Raman spectra of Cassiterite of samples A_12 and A_14 shows a strong peak at 634cm^{-1} , also proposed as cassiterite by (Liu et al., 2020). Corresponding photomicrographs shows that the encountered cassiterite impurities in samples A_12 and A_14 which are subrounded or angular; and the surface of the inclusion is smooth and undulate which is visible when using oblique light.

5.6 Silica/Quartz

- **Chemical Formula:** SiO_2
- **Microscopic Features:** Optical microscope analysis of sample A_06 shows that the observed crystal is opaque in natural. The crystal has smooth texture with shiny appearance and rounded in shape but unable to recognized with microscopic properties. Also, the examined impurity in sample A_17 is observed in dark greyish to blackish colour and does not exhibit pleochroism. Chalcedony belongs to the trigonal crystal system, like quartz, and is giving the homogenous appearance. Optically, chalcedony quartz exhibits very low birefringence, which makes it appear almost isotropic under polarized light. In general, it exhibits a waxy or silky lustre, giving it a smooth, lustrous appearance. Chalcedony is usually translucent, though some varieties can appear almost opaque.
- **Raman observation:** The sample A_06 examined through Raman spectroscopy shows that the impurity is Silica, corresponds to the Raman signature peaks in literature (Borowicz et al., 2012; De Wolf et al., 2003; Narayanan et al., 1997). It gives a clear single Raman peak,

of 519 /cm^{-1} . On the other hand, the Raman examination of sample A_17 and B_02 confirmed that the crystal impurity is a Chalcedony (Quartz) and Quartz respectively, according to literature (Angel et al., 2012; Tuschel, 2017). It gives a clear Raman spectrum, with characteristic peaks at 461 /cm^{-1} (Fig 5.8). The mineral impurity in A_17 is confirmed as Quartz-Chalcedony not the corundum (previously recognized). The chalcedony has prominent Raman peaks at 461 /cm^{-1} while the corundum has characteristics peaks at 380 and 416 /cm^{-1} .

5.7 Cryolite

- **Chemical Formula:** Na_3AlF_6
- **Microscopic Features:** Typically, cryolite exhibits several distinctive microscopic properties. Under plane-polarized light, it is typically colourless or greenish in colour and appears transparent giving glassy appearance. The observed crystal shows high relief with irregular boundaries. It is uniaxial negative. These characteristics are essential for identifying cryolite when observed under a polarizing microscope.
- **Raman observation:** The Raman spectroscopy indicates that the impurities in sample A_22 and B_01 are Cryolite. It gives a clear single Raman peak, of 555 /cm^{-1} (Fig 5.6). In sample A_22 the recorded impurity is previously identified as cristobalite, but the Raman reflection confirmed as Cryolite. This confirmation is based on Raman spectra because, both of minerals have overlapping optical properties. Both minerals are uniaxial negative and displaying glassy appearance. For both minerals, colour varies from colourless to greenish brownish. But the Raman spectra indicated that the impurity is cryolite and has prominent Raman peak, of 555 /cm^{-1} (Malherbe & Gilbert, 2013; Parker et al., 2020; Tan et al., 2020) while the cristobalite have Raman peaks of around 230, 417 /cm^{-1} . On the other hand, the impurity in sample B_01 is Cryolite, based on Raman spectra with prominent Raman peak, of 552 /cm^{-1} (Malherbe & Gilbert, 2013; Tan et al., 2020) while the standard Raman peaks for chromite are 550 and 685 /cm^{-1} (Lenaz & Lughi, 2013).

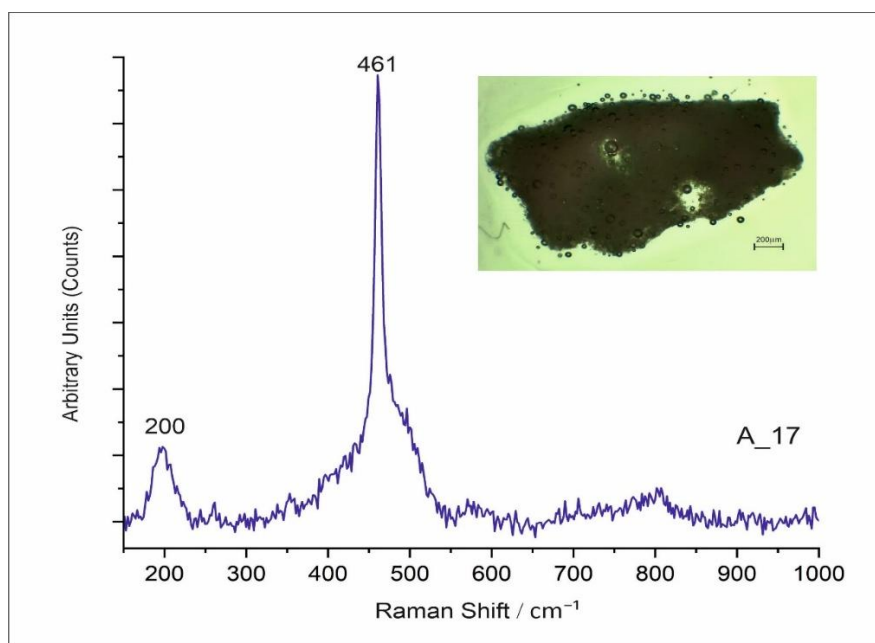


Figure 5.8 Raman spectra of a disordered quartz from studied sample in which the Raman vibrational modes are presented, along with photomicrograph of the quartz impurity with a semiopaque appearance and irregular shape.

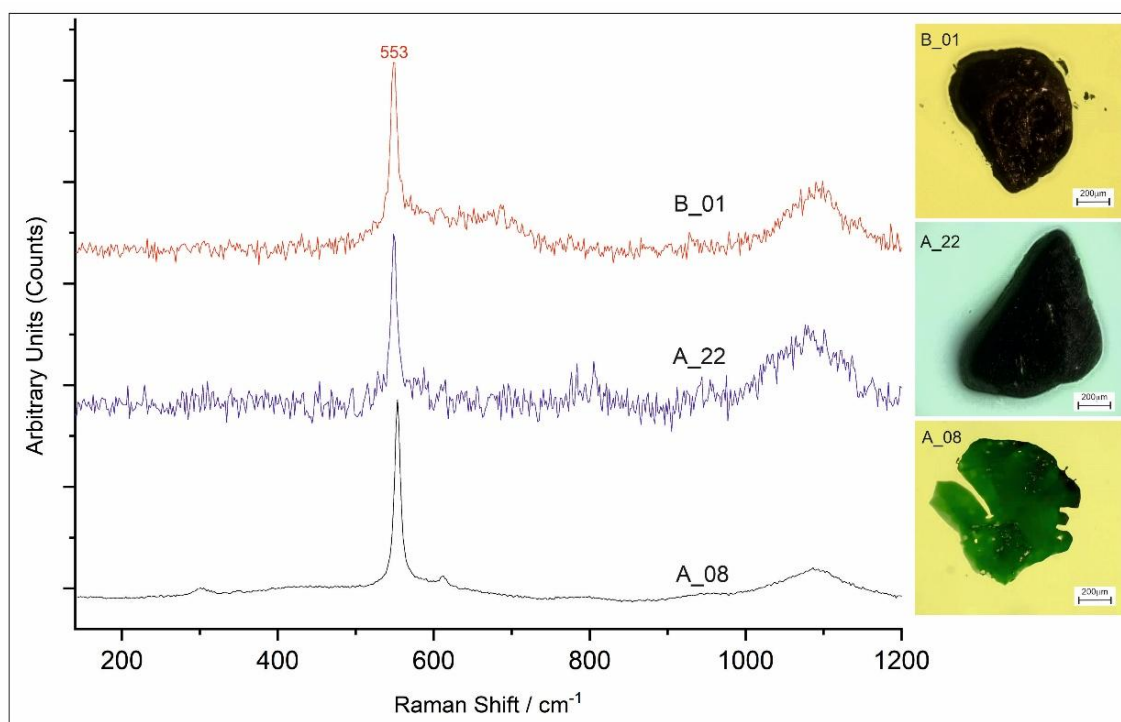


Figure 5.9 Raman spectra of cryolite from samples A_18, A_22 and B_01 having signature peak at $\pm 553 \text{ cm}^{-1}$. Corresponding photomicrographs show the encountered cryolite impurities from samples with a variable appearance. The identification of this impurity is challenging without quantitative Raman analysis.

5.8 Molybdenite

- **Chemical Formula:** MoS_2
- **Microscopic observation:** The observed grain appeared as an opaque impurity. Typically, molybdenite occurred as an opaque to dark lead grey in colour. Molybdenite is anisotropic, meaning its properties vary when measured in different directions. It shows strong anisotropic effects under reflected light microscopy, appearing different in different orientations.
- **Raman Observation:** The Raman spectrum confirmed that the crystal impurity in sample A_11 is a Molybdenite. It gives a clear Raman spectrum, with characteristic peaks at 390, 428, 466/ cm^{-1} (Fig 5.10). According to previous identification, the impurity is Carnegieite (NaAlSiO_4). Our confirmation is based on Raman spectra, as both the Molybdenite and Carnegieite have similar optical properties. The molybdenite is ore mineral of molybdenum and generally appears as opaque and is non-pleochroic. Carnegieite is typically colourless or white, though it can appear slightly tinted due to impurities and does not exhibit pleochroism. Additionally, the molybdenite observed in this sample have slightly displaced Raman peaks as compared to the standard from literature (Windom et al., 2011).

5.9 Wollastonite

- **Chemical Formula:** $\text{Ca}_3(\text{Si}_3\text{O}_9)$
- **Microscopic observation:** Typically, the wollastonite grain appears as a dark bead embedded in glass, exhibiting high relief and an opaque appearance. The grain appears as oval to acicular in shape.
- **Raman Observation:** The Raman examination confirmed that the crystal impurity in sample A_21 is a Wollastonite $\text{Ca}_3(\text{Si}_3\text{O}_9)$. It gives a clear Raman spectrum, with characteristic peaks at 638 and 972/ cm^{-1} (Böhme et al., 2019; Coentro et al., 2014) and as shown in (Fig 5.10). Wollastonite is a calcium silicate mineral and crystallizes in the triclinic system. Generally, wollastonite is uniaxial (+) and notable for its moderate birefringence. The mineral typically shows weak or no pleochroism. Previously this impurity was identified as devitrification product of standard soda lime ($\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$) glass composition according to Verallia identification.

5.10 Rutile

- **Chemical Formula:** TiO_2

- **Microscopic observation:**

Rutile is the most common naturally occurring titanium dioxide polymorph. Generally, its pure form is colourless or transparent. However, in nature, rutile often contains impurities that give it a range of colours. Another significant optical feature of Rutile is its strong birefringence, a result of its tetragonal crystal structure.

- **Raman observation:** The sample B_16 examined under Raman reveals that the impurity is a Rutile (TiO_2). It gives a nice Raman spectrum, with characteristic peaks at 240, 445, 608/ cm^{-1} (Fig 5.10). Rutile is the most common naturally occurring titanium dioxide polymorph and is widely distributed as an accessory mineral (Meinhold, 2010). It is one of the most stable heavy minerals in the sedimentary cycle, widespread both in ancient and modern clastic sediments (Maftei et al., 2020a).

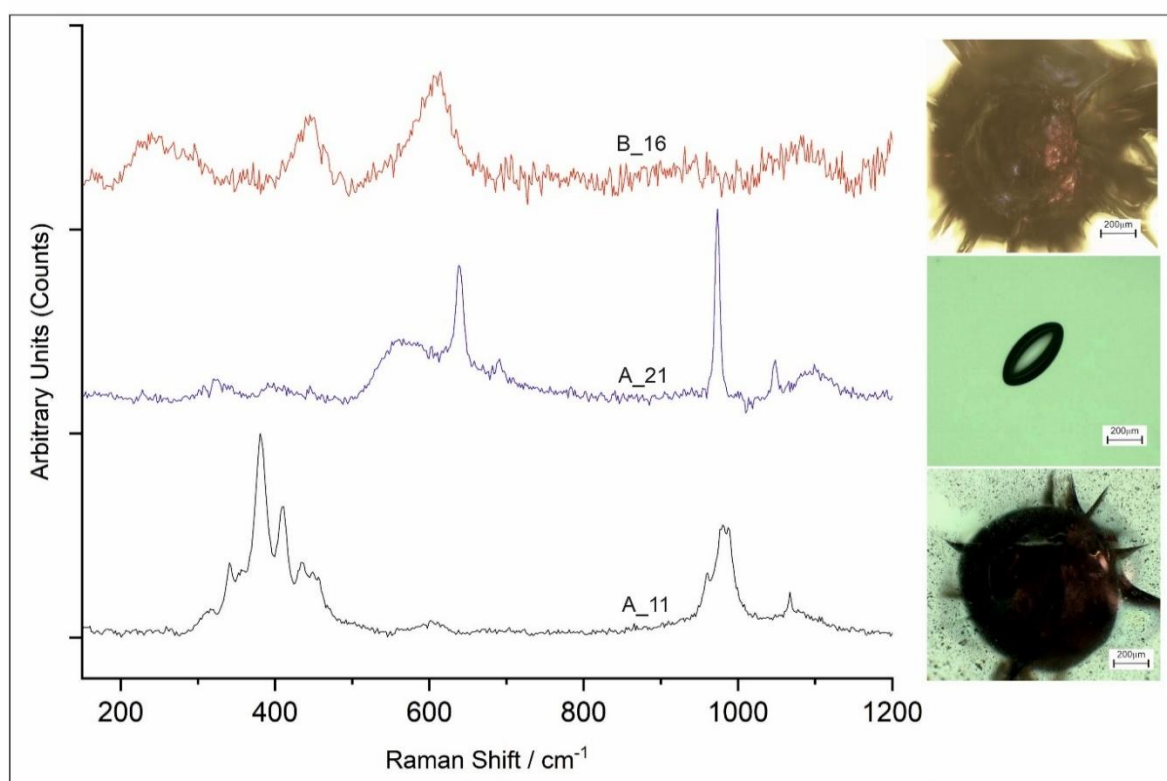


Figure 5.10 Stacked Raman spectra of molybdenite (A_11), wollastonite (A_21), and rutile (B_16) along with corresponding photomicrographs, recorded from the analysed glass samples. The Raman spectra show characteristic peaks for each mineral, while the photomicrographs illustrate the morphological variation.

5.11 Calcite, Dolomite and Anatase

- **Chemical Formula:** CaCO_3 & $\text{CaMg}(\text{CO}_3)_2$
- **Microscopic observation:** The impurity under the microscope appears in the form of bunch of thin snowflakes with bubbles embedded in glass. The boundaries are not clear and giving greyish colour if the green colour of glass is ignored.
- **Raman Observation:** Through Raman examination the spectrum confirmed that impurity is the mixture of carbonate which includes calcite and dolomite along with anatase. The characteristics peaks for calcite are 280 and $1086/\text{cm}^{-1}$, for dolomite peak at $1098/\text{cm}^{-1}$, while for anatase is $142/\text{cm}^{-1}$ (Fig 5.11). The optical property of the impurity is not clearly recognizable due to the appearance of the impurity. However, the Raman examination confirms that the mineral impurity is a mixture of calcite and dolomite. Calcite typically forms rhombohedral, scalenohedral, and prismatic crystals, and it can also occur in massive, granular, or fibrous habits. Optically, calcite is notable for its strong birefringence and is uniaxial (-). Dolomite is a common and important mineral in sedimentary rock formations, particularly as the primary component of the sedimentary rock known as dolostone. It crystallizes in the trigonal-rhombohedral system. Optically, dolomite is a biaxial (-) mineral with birefringence is lower than that of calcite. The impurity under the Raman gives the characteristics peaks at 280 and $1086/\text{cm}^{-1}$ which show the presence of

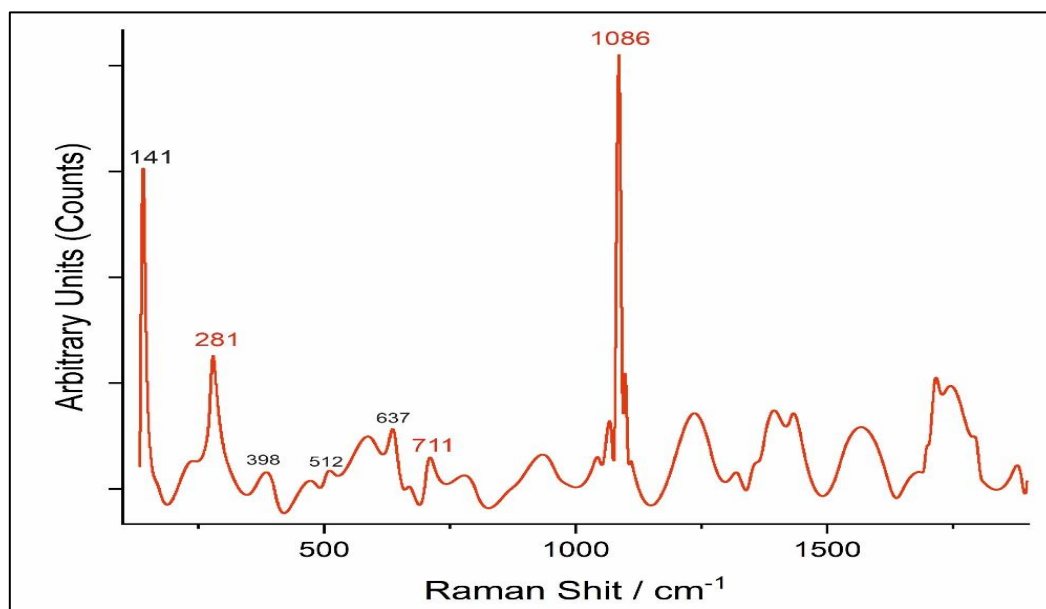


Figure 5.11 Raman spectrum recorded from sample A_19, demonstrating the presence of multiple impurities within a single glass cut piece. The peaks position indicated in black correspond to the characteristic Raman bands of anatase, whereas the peak position highlighted in red represents the presence of calcite and dolomite.

calcite (Donnelly et al., 2017; Kim et al., 2021; Sun et al., 2014) . The peaks at $1098/\text{cm}^{-1}$ indicates that the impurity may also contain the presence of dolomite (Sun et al., 2014) while the presence of anatase is confirmed by the peak $142/\text{cm}^{-1}$ (Kernazhitsky et al., 2014; Maftai et al., 2020b). The previous identification for this impurity, made by Verallia, shows that the mineral impurity is Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). Optically mullite is biaxial (+) and typically exhibits weak pleochroism. Generally, the characterises Raman peaks for Mullite are around 223, 600, 864 and $974/\text{cm}^{-1}$.

5.12 Molybdate

- **Chemical Formula:** MoO_4
- **Microscopic Features:** The observed grain under plane-polarized light shows brownish colour with a greenish hue due to being embedded in green glass. Molybdate appears rounded and has high relief.
- **Raman observation:** The Raman spectrum from sample A_05 confirmed that the crystal impurity is a Molybdate. It gives a clear Raman spectrum, with characteristic peaks at 321, 390, 793, 846, 878, 891, $973/\text{cm}^{-1}$ (Fig 5.12a). Chemically, a molybdate is a compound containing an oxyanion (an anion containing oxygen) with molybdenum in its highest oxidation state. Molybdenum can form a large range of such oxyanions, which can be discrete structures or polymeric extended structures. Examples of molybdate oxyanions are, Na_2MoO_4 and CaMoO_4 (mineral powellite). Here the recorded spectra depict the presence of the Molybdate specifically the CaMoO_4 (Thrane et al., 2020).

5.13 Selenium

- **Chemical Formula:** Se
- **Microscopic Features:** Selenium is a non-metal chemical element with symbol Se and atomic number 34. Selenium is a member of the selenium group. Under the microscope, the selenium grain appears greyish to greenish in colour, exhibiting a granular texture with no distinct boundaries.
- **Raman observation:** The sample A_04 analysed under Raman unveils that the impurity is Selenium with characteristic peak at $234/\text{cm}^{-1}$ (Lei et al., 2020; Nagar et al., 2022) shown in (Fig 5.12b). The Raman peak at 235 cm^{-1} is expected to be of both E and A1 stretching modes of trigonal selenium polymorphic structure (Kora & Rastogi, 2016).

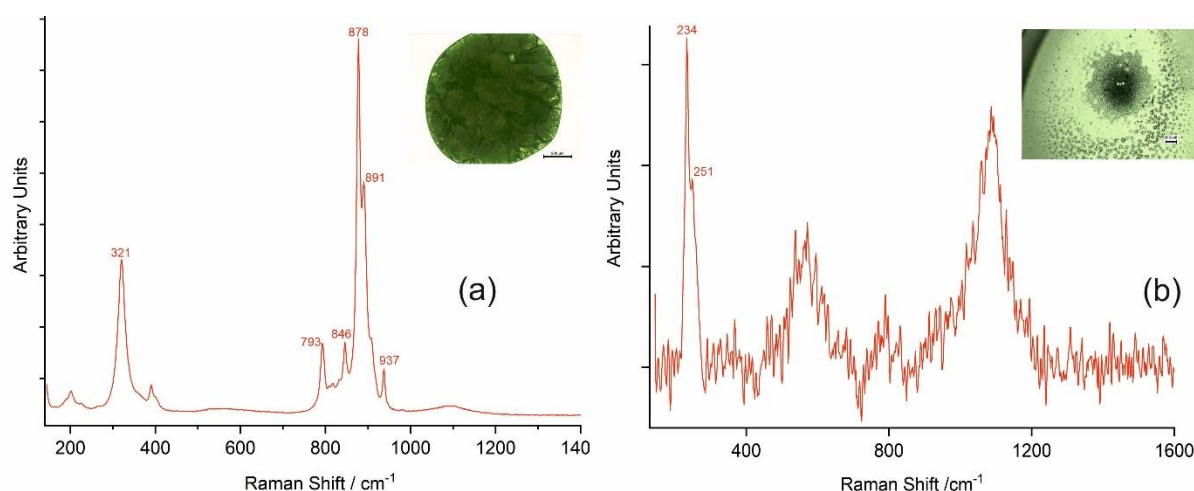


Figure 5.12 (a) Raman spectrum of a molybdate recoded from sample *A_05* showing the characteristics Raman vibrational modes, along with photomicrograph of the molybdate impurity. (b) Raman spectrum of Selenium with signature peaks at 234 and 251/cm⁻¹ along with photomicrograph.

5.14 Unknown Spectra

Despite the overall high quality of the Raman spectroscopic analyses and the successful identification of the majority of samples, a limited number of spectra could not be conclusively assigned as shown in (Fig 5.13). These unidentified spectra did not match any entries within the reference database developed at the Laboratory of Provenance Studies, University of Milan-Bicocca, nor did they correspond to spectra available in the RRUFF database or those reported in the existing literature.

However, it is important to note that the proportion of such unidentified spectra is minimal when considered relative to the total number of analysed samples. This suggests that the applied analytical approach and reference frameworks are robust, with only a marginal fraction of data remaining unresolved.

5.15 Discussions

The identification of inclusions within the glass matrices of the final glass products remains a challenge when depending only on the use of optical microscopy. As a result, traditional optical microscopic inspection employed nowadays in glass industry for quality control leads to uncertainty or misinterpretation. Using the real encountered inclusions from final products (green and amber-green bottles) of glass industry, we accurately applied our Raman spectroscopic method and identifies a multiple set of impurities, including corundum, baddeleyite, cristobalite, quartz, molybdenite, wollastonite, rutile, and glass inclusions. Several inclusions exhibit different appearance but share similar Raman vibrational modes, while other display nearly identical optical and morphological characteristics but corresponds to different minerals.

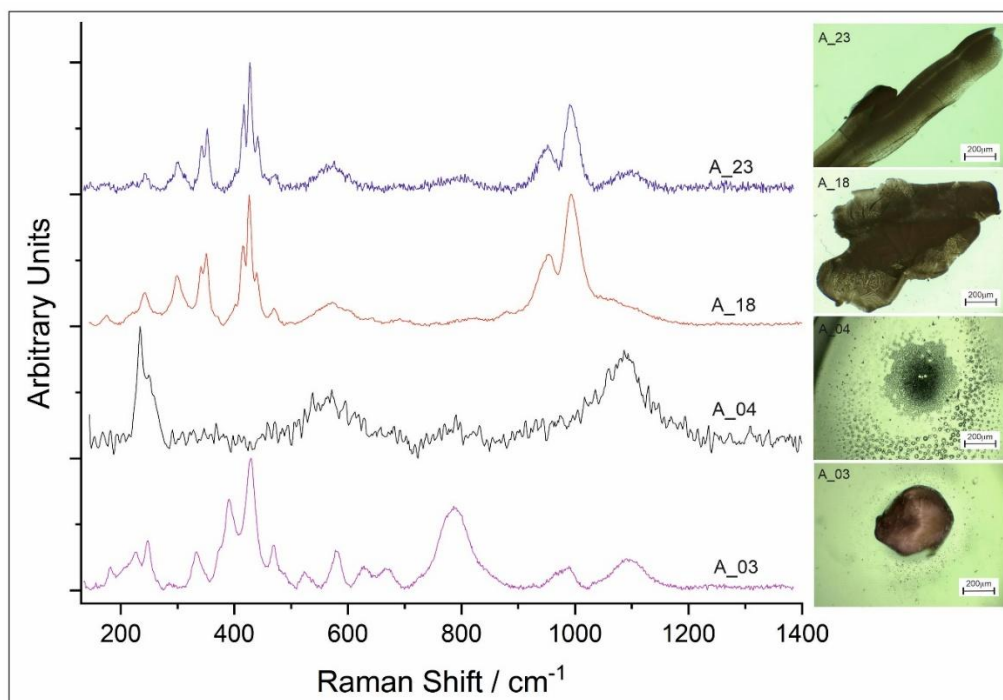


Figure 5.13 Stacked Raman spectra of the unknown recorded impurities. The sample A_03, rounded, eroded outline and in dark brown colour, with Raman spectra consistent with perovskite(?) in the reference database. In sample A_04 is the peak at 235, 231 corresponds to selenium(?). the Raman spectra of sample A_18 and A_23 display greenish brown colour with irregular and elongated shape morphology respectively, showing unknown similar Raman spectrum.

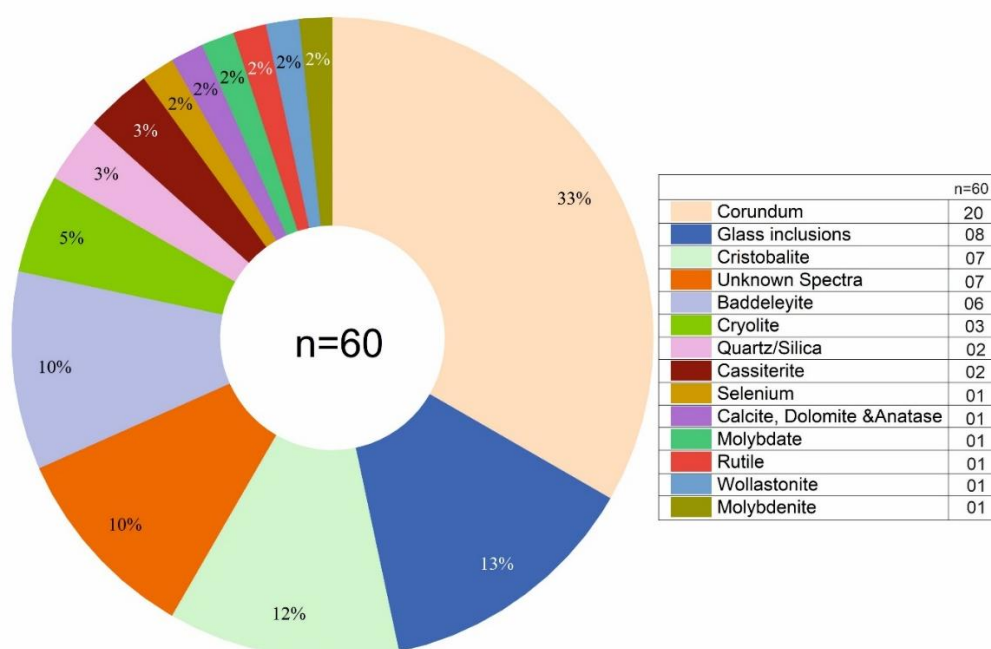


Figure 5.14 Relative percentage of encountered impurities in the (n=62) studied glass samples. The table reports the frequency indicating how many times each impurity appears within the total data set.

For example, four recorded baddeleyites inclusion have highly variable appearance but similar Raman spectra. On the other hand, the baddeleyite in sample A_01 and corundum in sample A_02 appears morphological similar under the microscope, but the Raman analysis indicates that they are two different impurities. This example clearly illustrates that when an impurity cannot be reliably recognized, effort aimed for its removal or source identification become significantly challenging. Additionally, another significance of the technique is that it offers the capability to distinguish between different polymorphs. For example, in our study we were able to successfully identify both quartz and cristobalite from different samples using this approach. By using this technique, we made many improvements from the previous identification made by operator using only the microscope. In this way the database of inclusions in glass could be updated accordingly, resulting in improved accuracy and precision. Additionally, it is important to note that further investigation is required for few of the unknown Raman spectra's which did not correspond to any reported spectrums from the data base we used or from the literature.

6. Conclusion

From the results, it is concluded that it's possible to apply this technique to examine the heavy minerals as the impurities in the quartz rich sand. The predominant heavy minerals identified are zircon, rutile, apatite, tourmaline, andalusite, muscovite and kyanite which represent potential impurities that could impact both the purity and coloration of transparent glass. The presence of these minerals, even in minor amounts, underscores the need for careful assessment and processing of raw quartz sand to minimize contamination and maintain high-quality standards in glass manufacturing. This technique applies to both the raw materials already in use and for the new quarries.

From the results it is also concluded that the application of Raman spectroscopy in this study demonstrates a significant improvement over previously used conventional optical microscopy method, in which shape, size, colour and other optical properties was used for identification. Due to the inherently low Raman scattering of glass, the spectra of the inclusion can be recorded directly, rapidly, and non-destructively. This study proposes a new method to determine the mineral impurities encountered in glass industry, which allows the users to identify these mineral impurities as inclusion more speedily and conveniently and to be identified regardless of the operator's experience. Also, this technique can serve as a primary, frontline analytical tool for a rapid identification during the production and in-situ analyses to check the quality of the production in few minutes. Timely identification of contamination is essential to identify the source of the contaminants, detecting if they are from raw material, from the refractory lining or from glass cullet and possibly correcting or eliminating the problem at the outset, improving the process. The main conclusion that can be drawn from the results of the all the identifications, made in this study, through Raman spectroscopy shows that the deployed technique is fruitful and can be routinely and successfully applied to glass industry. By applying Raman spectroscopic technique, the rapid identification of these impurities is possible because this technique is not invasive and non-destructive and needs no sample preparation, making the technique applicable to any trained operator.

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