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THESIS

Silica Sand in Construction

A case study from Skala, Kefallinia Island, Ionian islands, Greece

Dafni Kontopanou

Supervising Professor: Dr. Michael Stamatakis

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1.INTRODUCTION

AIM OF THE STUDY

The present Thesis has been accomplished through the Undergraduate Program of "Geology and Geoenvironment". The aim of the thesis is to examine the existence of silica sand, at Skala region in Kefalonia Island and to figure out its suitability level for construction uses. The material had been also extracted during the past, around 1980, by TITAN SA and AGET Hercules SA cement companies.

According to TITAN SA, 6.000 tons of silica sand was extracted every year from Skala region in Kefallinia Island. This amount of sand was concentrated at the cement factory of the company at Rio, in Peloponnese region, until 1985. Since then the place has been almost abandoned, with terraces that cover the old extracted area. Two main quarries have remained untouched so that we have a picture of how the place used to look like.

At the current study, quantities of Pleistocene silica sand were collected from the wider area of Skala and specifically from past sand-quarries and from areas which are located regional of these old extraction sites. The analysis of the samples has been done at the National and Kapodistrian University of Athens and at the Technical University of Athens. The purity of the samples in silica content has been examined through the mineralogical analysis of the samples, the determination of the carbonate free fraction and other impurities that influence the quality of the sand, regarding the uses in the construction industry. To figure out the SiO_2 and $CaCO_3$ content, as well as the clay mineral content and impurities, X-Ray Diffraction, Stereoscope and Sieve Analysis were carried out.

2. SILICA SAND

2.1 Characteristics

The most common elements involved in the earth's crust, silicon and oxygen, compose silicon dioxide union (SiO_2). This is the chemical formula of a group of minerals that are composed of these two elements (Kamar, 2004).

In nature, silicon dioxide occurs with many forms and polymorphs. Some of them are crystal quartz, cryptocrystalline chalcedony and amorphous opal (tridymite or cristobalite). Quartz is an abundant mineral that occurs in igneous (mainly granitic), metamorphic and sedimentary rocks (Bates and Jackson, 1984).

Quartz is colorless or white and sometimes it is colored by impurities, such as iron. It has got numerous varieties and an abundance of byproducts. In addition, quartz is one of the little minerals that survive from transportation, weathering or diagenesis, because of its hardness owed to the bonds between the atoms, thus it is involved in most of the sands (Kamar, 2004).

Sand is composed of fragments and grains of rocks and minerals. The main component of sand is quartz, but it can also involve alumina, feldspar and iron minerals. Silica sand is defined as broken quartz into tiny granules. The work of water and wind separates silicon dioxide from the mother rock, resulting to the production of silica granules which are transported and shaped over the time (Kamar, 2004). Silica sand has a wide range of uses such as the stone on the bed of a road, it is also the leading product in glassmaking industry or it could be used for making a computer chip. There are also a lot of other ways that silica can be used in construction, in cement and mortar mixtures (Kamar, 2004).

2.2. Genetic Types

2.2.1 Aggregates

Aggregates are distinguished in two categories. The first one and most common category is the one of Natural Occurring Aggregates. In this category crushed stone, sand and gravel is the main source of the material. Bedrock weathering and fragments' transportation followed by water or glacier deposition produce natural occurring aggregates. As such, the areas related to that type of deposits are rivers and streams, as well as glaciated areas. The crushed material can be produced by a variety of bedrocks (Langer, 1988). Natural aggregates do not only involve of stable rock, but they also consist of sand size particles. Grain size is important to categorize aggregates in sands or gravels. Quartz usually dominates in sand deposits, because of its

durability (Prentice, 1990).

The second category of aggregates is the Marine Aggregates defined as non-metallic accumulations of sands, gravels, shells or coral debris which are formed on beaches and in the offshore areas. All of them are included in the EEZ (Exclusive Economic Zone) deposits. The source of marine aggregates is the changes of the sea-level during Pleistocene, due to glaciation withdrawal and eustasy. The transportation and reworking of glaciers in middle and high latitude continental shelves produced quartzite, flint and chert rock fragments that can be transported for long distances without be destroyed. After the ice melted minerals and rock fragments of each size were deposited. Glaciation melting resulted to sea-level rise, which made the formation to be reworked. Aggregates were redistributed through reworking processes. Waves and tidal currents are the main factors of transporting aggregates. Their distribution reflects how the source material reacted during deposition under a specific energy level (Cronan, 1992). Seafloor hydrodynamic processes concentrated marine aggregates at their present place, however their mechanism of deposition is closely related with glaciers and rivers. On modern beaches the production of aggregates continues through the erosion of local continental material that adds much of the aggregates on the beach (Cronan, 1992).

2.2.2. Sand and Gravel

Sand and gravel have a suitable size to be used directly or it needs a minimal process as they have been already processed naturally. This can downsize and categorize them in groups of the same size grade. In the end there are different sizes of them, such as boulders and cobbles, that need to be reduced to be useful in construction. Also, they occur as pebbles that are used directly (Prentice, 1990). The characteristics of the grain size are extremely determined by the method that sand and gravel are formed. The main factors that are responsible for the size characteristics of the sediment are the following ones: i) the sedimentary source area and ii) its weathering level influence the petrology and the shape of the clasts. Depending the type and the distance they are transported the clasts are shaped and distinguished from the softer ones. The last factor, that affects further the shape and the diversity of final deposit, is the depositional process. It is very important to know the formation processes to know exactly their properties and exploit them efficiently. So, there are categories for each deposition mode such as alluvial, colluvial, glaciogenic, marine and residual deposits (Prentice, 1990).

A significant source of sand and gravel is the alluvial plains of the rivers. They are streams with high velocity that carry sand and gravel. The aggregates are poorly sorted, taking an angular shape and sometimes they are followed by silt and clay (Harben and Kuzvart, 1996). When large

rivers flow slowly they can transport only fine silt and sand. That is what happens at the present, although during Pleistocene much more of material was transported enhanced by higher velocities. A river sequence can be complicated as it relates to the flow rhythm. It consists of a gravel channel at the bottom and above it there are different terraces (Prentice, 1990).

Another source of aggregate material is the colluvial term, which has to do with mass movements (Prentice, 1990). The mobilization material is regolith or the in-situ bedrock. Flows and creeps are associated with the gravity that is influenced by stress-strain relations and pore-water (Millar, 2014). The material is transported by sliding from slopes that belongs to, so the final formation is petrographically like the origin rock. They were formed in steep slopes during Pleistocene glaciations and they are covered by vegetation at the present (Prentice, 1990).

Glaciogenic sand and gravel is another type of aggregates that derived from ice sheets movements, which carried boulders, cobbles, pebbles, sand, silt and clay. When the ice caps melted, they were discharged, and all these materials were deposited in situ. This deposit is dominated by clay which cannot be removed by processing so that it could be useful in construction. Although in some cases, where the water produced by ice melting flew slowly, clay and silt were transported for long distances leaving behind clean sand and gravel that are characterized as fluvioglacial and they have a wide range of size (Prentice, 1990).

Marine deposits are also a source of sand and gravel that defers to the land formations. For all the rock fragments erosion, that works on the land and results in the sea, is responsible for their production. Clasts larger than fine are not allowed to be transported as the sea water moves slowly. Another thing that characterizes this type of deposits is the constant move of the sea water. The fragments are moved in short distances and they can also stay untouched for years. The biggest advantage of marine deposits is the low silt content; however, salt and shells are factors that contaminate the deposit and need to be removed. Salt destroys cement when it is not washed and removed from the deposit and shells have calcium carbonate composition which reduces the quality of the concrete (Prentice, 1990).

Residual deposits are a situation that sand, and gravel formation has not been transported. This is called in situ formation, in which the main depositional factor is weathering both mechanical and chemical. The upper part of the rock, the one that is in contact with atmosphere, breaks in depth. This is how a weathering mantle is formed that involves coarse aggregates. Residual deposits have been also formed in areas that high evaporation of water from the surface occurred and there was a transportation of groundwater. This formation can be developed as very thick layers that constitute a main source of coarse aggregate in many parts of the world, that no other source exists. It is called duricrust and depends on the soluble of the ground water and the geology that allows the circulation (Prentice, 1990).

2.2.3 Sandstone

The depositional environment is the one factor that determines the mineralogy of sandstone. Differences between environments are followed by changes in the sediment composition. The volatility in rock fragment content is what reflects the ability of unstable grains to survive which affects the composition of sandstone in each environment. In addition, textural changes can result in composition changes (Davies and Ethridge, 1975).

So, the composition of sandstone is compiled by a mixed combination of materials. The components of the sandstone can be organized in a triangle shape. At one part of it there is quartz, 25% feldspar, rock grains and matrix. This composition is recognized as graywacke. It is not much sorted which reflects a rapid rhythm of sedimentation. Another composition of sandstone is arkose sandstone in which quartz and feldspar grains dominate and cement is less as a mineral precipitate. The third type of composition is defined as orthoquartzite in which the higher percent of the grains is quartz and it is at least 95% (Harben and Kuzvart, 1996).

Orthoquartzite derives from the reworking and the alternation of the sediment processed by waves when almost all the minerals are removed or destroyed apart from the stable ones such as quartz. It is also known as quartz arenite. Quartzite is another byproduct of sandstone, the purest one, produced by metamorphism of quartz arenite. It is extremely cemented, and the quartz particles are indurate (Harben and Kuzvart, 1996).

2.2.4. Crystal Quartz

Crystal quartz takes place in sedimentary and igneous deposits. In sedimentary rocks it is related with colluvial, alluvial and residual deposits but the main source of material is the major crystal quartz formation. In igneous rocks it can be formed in cavity-rich pegmatite veins and in hydrothermal mesothermal deposits.

Cavity-rich pegmatite veins are formed in the endo-contact of granite bodies which are rich in quartz. Hydrothermal mesothermal deposits with quartz quantities are defined as ore-free veins developed in siliceous rocks such as quartzites, mica-schists and granites. The mother rock is the main source of SiO_2 that produce veins and crystal cavities (Harben and Kuzvart, 1996).

2.2.5 Tripoli, Novaculite, Flint

Chert is a term used for all sedimentary siliceous deposits that have been lithified under silica redistribution. All the three types of deposit (tripoli, novaculite, flint) describe different varieties of chert, which is a microcrystalline or cryptocrystalline sedimentary rock characterized by high density and hardness and involves crystals of quartz less than 30 µm in diameter (Harben and Kuzvart, 1996).

Tripoli is a name given to a diatomaceous deposit that was found on the North African coast. The deposit is fine-grained (less than 0.1 to 7 µm) siliceous relics derive from siliceous limestone or thick beds of chert that are affected by leaching or weathering. Also, the dissolution of soluble alkalis of a colloidal silica and alkaline salts formation transits silica resulting to tripoli deposition. It is microcrystalline and characterized by high content in silica (98-99%), softness, fragility and porosity (about 45%). It also includes a low percent of alumina, titania and iron oxide, which affects the color of the rock. The color varies from white or yellow commercially known as "cream" to brown to red known as "rose" (Harben and Kuzvart, 1996).

Novaculite is a sedimentary rock found in Arkansas and Oklahoma which can have been formed by different processes, such as the precipitation of silica through chemical or organic agents, replacement of non-siliceous deposits, or recrystallization and silicification of volcanic products. Diageneses and volcanism far from accumulations of silica particles can affect their texture (Harben and Kuzvart, 1996).

It is composed of microcrystalline quartz and it is also characterized by hardness and high density. It is very resistant to erosion and it has thin and sharp edges. Its color ranges among white to grayish or black. The thickness of the formation can diverse from 75 to 275 meters (Pennington, 2013).

Flint is not so common in layered deposits and bedded chert. It occurs mostly as nodules or concretionary segregations in limestone or dolomite. It is lithified by redistributed silica because of metasomatic replacements of limestone. It is dominantly composed of very small-sized silica crystals, a part of them derives from organic opal, and it is free from calcium carbonate. It is very hard and compact, and it often includes organic particles such as sponge spicules and fragments of brachiopods, that can be easily distinguished by bigger crystals (Harben and Kuzvart, 1996).

2.3 Industrial Uses

The industrial sand that is used in manufacture and industry need to be pure in SiO_2 proportion up to 95% and composed of more precise granules. The bonds between the atoms make silica a hard and chemically inert product, which is not easy to be melted (Kamar, 2004).

It is used as an alternative material for concrete increasing its workability and enchanting the compressive and flexural strength. It has also applications in foundries and filtration systems and when quartz is transparent to translucent it is used in glassmaking and ceramic industry (Kamar, 2004).

The combination of silica sand's strength, silicon dioxide and non-reactive properties makes it an essential ingredient which takes part in the production of uncountable every day products (Kamar, 2004).

General uses of silica sand in the production of every day products are developed in the next units.

2.3.1 Construction

In construction grain silica is used as primary structural component in flouring compounds, mortars, cements, stucco, and asphalt mixtures. It provides durability and flexibility and it protects the construction from a possible corrosion or weathering (Kamar, 2004).

Silica sands worth to be used in construction because of the combination of physical and chemical properties. The high content in quartz combined to a low level in impurities, clay level, iron oxides and chromite, makes them very special. The range of grain-size distribution is short (around 0.5 to 0.1 mm). However, each application demands a different combination of properties (DCLG-BGS Joint Minerals Information Program, 2009).

2.3.1.1 Mortar

Mortar is composed of sand cement and a mixture of water, which hydrates the cement and holds the mix together. Mortars involve a lot of water compared to the proportion of water in concrete. The mixture that is produced is a thick substance in a glue form that can be used for building materials such as bricks (Penetron Hellas, 2018).

Every type of quartz aggregate, such as quartz powder and industrial sand or quartz sand mix, are very important for mortars in construction. Quartz materials aim to make mortar harder enhancing its traction to improve the workability, the slid ability and the color. It has been

proved through studies that quartz aggregates improve the interrelation between the components of mortars and additionally the different proportions of silica aggregates produce different type of mortars (Penetron Hellas, 2018).

A good mortar quality depends on its chemical and physical properties. That means that the produced material will adhere firmly to the surfaces that it is applied, and it will preserve its hardness and durability under the atmospheric influence (Tweeddale, 2019).

The value of silica sand as a compound in mortars can be better understood by comparing characteristics and differences between lime and cement mortars but also among different types of cement mortars. The main difference between the setting of silica sand mortar and lime mortar has to do with the mass of mortar because of chemical changes. Lime mortar is set due to the absorption of CO_3 from the atmosphere, which later gets connected with the calcium of the hydrate lime, expulsing water at the same time. The expulsion of water provides gradual hardness to the substance from the outside to the inward to diminishing rates. Because lime mortar dries slowly and diminishingly it needs a dry environment to expulse all the water it consists, thus it is not suggested for under water masonry (Tweeddale, 2019).

According to Retno Setiati research (2017), "The potential use of silica sand as nanomaterial for mortar", silica sand when it is processed into nanomaterial affects the mechanical properties of concrete. A nanomaterial is characterized by physical, chemical and biological properties which can change significantly when the dimensions of the material are in nano-scale (particle size between 1 to 100 nm). Cement structure is not compact, little pores much smaller than the cement sized particles exist between them and they cannot be filled by cement sized grains. The only particle size that can fill them is fine dust nano-scale size. In the following picture is interpreted the structure of a cement mesh, filled by nano particles. It has been observed that when they are involved in concrete they provide higher density by reducing the number of pores.

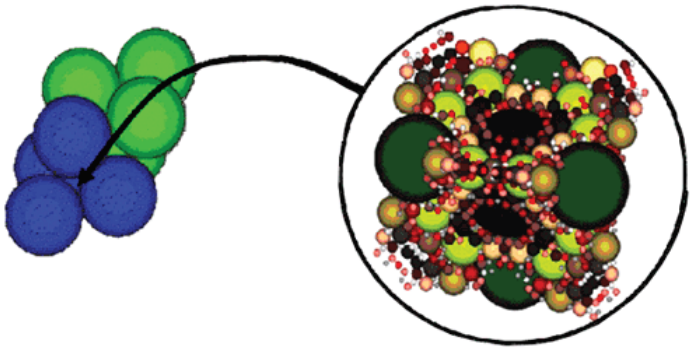


FIGURE 1. The concept of filling pores in concrete by nanomaterial (Schmidt, 2007).

Silica sand transfuses to concrete better characteristics than the conventional ones. It affects increasingly the compressive strength and the density, as well as the permeability. However, the major factor that determines the use of silica sand as nano-material is its content in SiO_2. When silica sand is pure in SiO_2 (above 99%) it has the potential to be nano-silica (Setiati, 2017).

2.3.1.2 Cement and Concrete

Cement can be made of limestone, clay, shells and silica sand and it is used in construction as a binding material. Concrete is composed of cement, sand, gravel or coarse aggregate. Consumption and construction industry demand bigger production of concrete so there is a depletion of natural aggregates as well as emissions of a huge amount of CO_2 in the atmosphere. To reduce the burden of the environment there has been suggested supplementary materials so that the cement consumption can be reduced (Chaudhary et.al, 2015).

Silica sand is one of these materials as it occurs naturally in abundance and it is low priced. A lot of research has been done around the alternative uses of silica sand in concrete industry the last fifty years (Jignesh and Vaniya, 2015).

Studies showed that silica sand can replace natural aggregates as a fine aggregate material. The raw material is a source for silica sand and they separate each other by washing. The clay material is taken out of the raw material, which is clean and involves only different size of silica sand that can be separated by different size of sieves. Each size category of silica sand is used for different applications in construction. For example, for concrete making, as partial replacement of fine aggregates, it is used sand size 1.18 mm to 60 microns (Jignesh and Vaniya, 2015).

The results of experiments in which concrete was replaced by silica sand showed that the compressive strength is influenced by the addition of different proportions of silica sand. Depending of the amount of silica sand, the compressive strength can increase or decrease. For example, in the cases that the added quantity of silica sand is until 30% or between 50-70%, the compressive strength is increased otherwise it decreases (Jignesh and Vaniya, 2015).

2.3.1.3. Foundry Sand

Foundry sand is high quality silica sand that is used in metal casting. It is the byproduct of ferrous or non-ferrous casting industry. The advantage of this sand that has been used in foundries is the potential of recycling it and reusing it many times in the production. The main use of it is as molding material which forms bricks and cores (American Foundry Society).

The grain size distribution of foundry sand is mostly between 0.6 mm and 0.15 mm sieve sizes, but it can also involve smaller particles than 0.075 mm. the grain shape is usually subangular to rounded. Additionally, foundry sand has a low level of absorption, however this varies accordingly to the presence of binders and additives. Sometimes foundry sand includes organic quantities, which are useful in applications where organic impurities are necessary. A spent foundry is dominantly composed of silica, a thin layer of carbon, a binder substance (bentonite or coal) and dust (U.S Department of Transportation, Federal Highway Administration).

When sand has been used in many production cycles and it can no longer be reused, it is moved away from the foundry and characterized as foundry sand. The casting process and the origin of the sand are the two factors that determine its physical and chemical characteristics by the end of its use in the foundry (Siddique et.al, 2007).

The categories of foundry sand depend upon the fusion system in metal castings. There are two types of binder systems involving either foundry sand classified as clay bonded or as chemically bonded. Both are appropriate to be used, although they have different physical and environmental characteristics (Siddique et.al, 2007).

Studies showed that when foundry sand is involved in concrete mixtures, it provides higher compressive strength, splitting-tensile strength, flexural strength and elasticity. All the above characteristics that concrete gains through the contribution of used-foundry sand, suggest this sand in making construction materials and concrete mixtures (Siddique et.al, 2007).

2.3.2 Beach Nourishment

In our days, the most preferred way to deal with erosion problems of sandy beaches is a process called Beach Nourishment (Mabin, 1991). The sandy part of the beach is removed due to wave action and erosion, something that decreases the width of the beach and sometimes it is dangerous for the local communities close to the coast. According to this method of confrontation the coast is nourished with sand, transported from different areas that have surplus of the material or from the bed of the sea after the 15-meters-depth (Mesochoritis, 2018). Before the borrowed material is added on the beach it has to be checked for involved heavy pollution, metals, organic material and hydrocarbons. Moreover, clay material should be removed (Rapada, 2015). The sand material is placed so that the coast is expected to the sea. Usually the level on which the extra material is added is 1 to 2 meters higher than the sea level. After the deposition, waves arrange a balanced situation of the material (Mesochoritis, 2018).

Previously, that kind of problems were usually faced constructing rigid structures such as, groynes, seawalls and coastal revetments. The old dealing way was partially more expensive, because replenishment's sustainability demands higher budget, although the most important is all the previous types of construction, protecting the coastal zone, were not in harmony with the

entire environment of the coasts (Mabin, 1991).

According to a research about the 'Feasibility Evaluation of Upland Truck Haulas as a Beach Fill in Construction Method in Broward Country, FL- Segment II' potential sources of the replenishment material should be selected according to the sediment characteristics and its compliance with the quality guidelines and the location for possible methods of transport (Olsen Associates, 2012). The research also showed that borrowed sand with larger grain size than the one at the beach was more stable and less likely to be removed by tidal and wave action. Moreover, sand with low fine contents also performs well (Olsen Associates, 2012). Other researches came up to the same conclusion as well, summing up the two most important factors for selecting the nourish material for each beach. The first one is the erosion level of the beach and the second one is a suitable borrow area (Mabin, 1991). The source of the borrowed material should have, if not the same, similar characteristics, composition, size and sorting characteristics with the beach. Although as it is difficult to achieve the perfect matching of the borrowed sand with the beach sand, it is preferred to borrow and add, in general, coarser sands compared to the eroding matter of the beach in order to be stable for a longer period. Furthermore, finer material replenishment is avoided, since it will be eroded in a short period. It should also be close enough to the replenishment area in order to be valuable the transportation on the material compared with the nourishment process (Mabin, 1991).

For local authorities and tourist resort operators silica and quartzose sand is usually preferred for the beach nourishment. That kind of sands offers a bigger buffer zone between the sea and land, which protects from erosive events and provides safety. At the same time the quality and the amenity of the beach are better improved (Mabin, 1991).

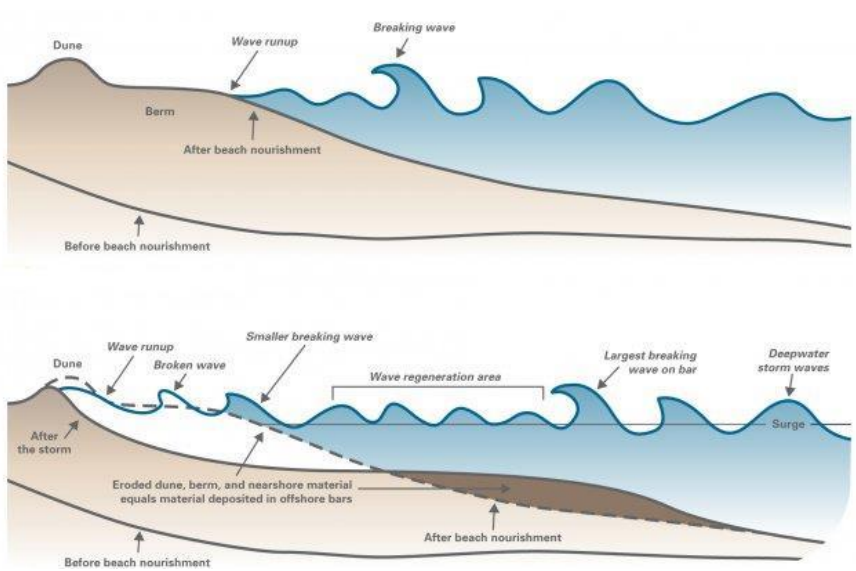


FIGURE 2. Storm results before and after Beach Nourishment (Rapada, 2015).

2.3.3 Glassmaking

Silica sand is a material that can be found in all the major types of commercial glass. In glass construction any glass-grade sand should be cleaned by impurities of Fe_2O_3 content involving at least 0.008 % of it and controlled by other components such as Al_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, ZrO_2 and Cr_2O_3. That means, the sand must be pure in silica around 98-99%. Other trace elements that may be involved, such as nickel, copper or cobalt, can produce color or deteriorate the quality of the glass (Harben and Kuzvart, 1996).

There have been established three main categories of glass products to make clear the permitted iron content. Those are the colorless container glass (flint glass), the clear flat glass and the colored contain glass. Silica sand provides the major component of SiO_2 which purity determines the color, the clarity and the strength of the glass (Kamar, 2004).

2.3.4 Ceramics and Refractories

Ground silica is very important for the main body and the glaze of every type of ceramic products, including products such as tableware or floor and wall tile. It is a structural factor on which clay and flux are added. The SiO_2 is used to regulate thermal expansion and to control drying and shrinkage. It is also important because it enhances the structure and the appearance of the products (Kamar, 2004).

Apart from regular silica sand, its byproducts can be used as an essential source of silica in ceramics industry. For example, flint that has been exploited in UK, provides good thermal behavior and resistance (Harben and Kuzvart, 1996).

The durability of quartz makes it a useful material for refractories, as quartz never breaks down extremely no matter how high the temperature is. Quartz can be converted in different forms as the temperature increases. It is stable until 1,470°C where it is transformed to cristobalite which stays stable to 1,700°C. Thus, it is used as silica brick, which is produced by crushing orthoquartzite or metaquartzite to coarse sand size. It is mixed with water, lime and organics, casting into bricks and firing until it reaches a temperature of 1,540°C (Harben and Kuzvart, 1996).

2.3.5 Filtration and water production

Water filters are designed to remove whatever contaminate and deteriorate the drinking and wastewater. They are made to protect its chemical composition from materials and algae that consists fine grade sand and gravel. For this reason, they are constructed with three graded layers at the bottom of silica sand. The water is driven from the top to the bottom so that the larger sized particles stick at the top layers of sand and the smaller ones such as organic sediment are left in the sand filter, where they are consumed by micro-organisms (bacteria and protozoans). When silica sand has a grain size around 0.1 mm in diameter removes every residuum, coliforms and viruses (Harben, 2002).

Industrial sand has the above characteristics, because its distribution of the gain shapes and sizes provides an efficient filtration bed. Silica is chemically inert, thus it will not deteriorate the quality of water and additionally it will not react with acids, organic matter or solvents, when they will be in contact (Kamar, 2004).

2.3.6 Metal casting and metal production

In metal factories the cores and the molds are composed of high-silica sand (industrial sand) bonded with clay or blended with sodium silicate. Cores and molds are stable because of silica's high fusion point and limited thermal expansion. Silica that is used in metallurgy must be very pure (98% SiO_2), otherwise it enables gases to escape. (National Industrial Sand Association). The proportions of SiO_2 result from chemical analysis, particle size and shape distribution. Some uses of silica in metallurgy are as a fluxing agent in soldering fluxes, as a flux in smelting base metal ores (separating oxides from the base metal), balancing the lime or as abrasive (Harben and Kuzvart, 1996).

2.3.7 Oil and Gas Recovery

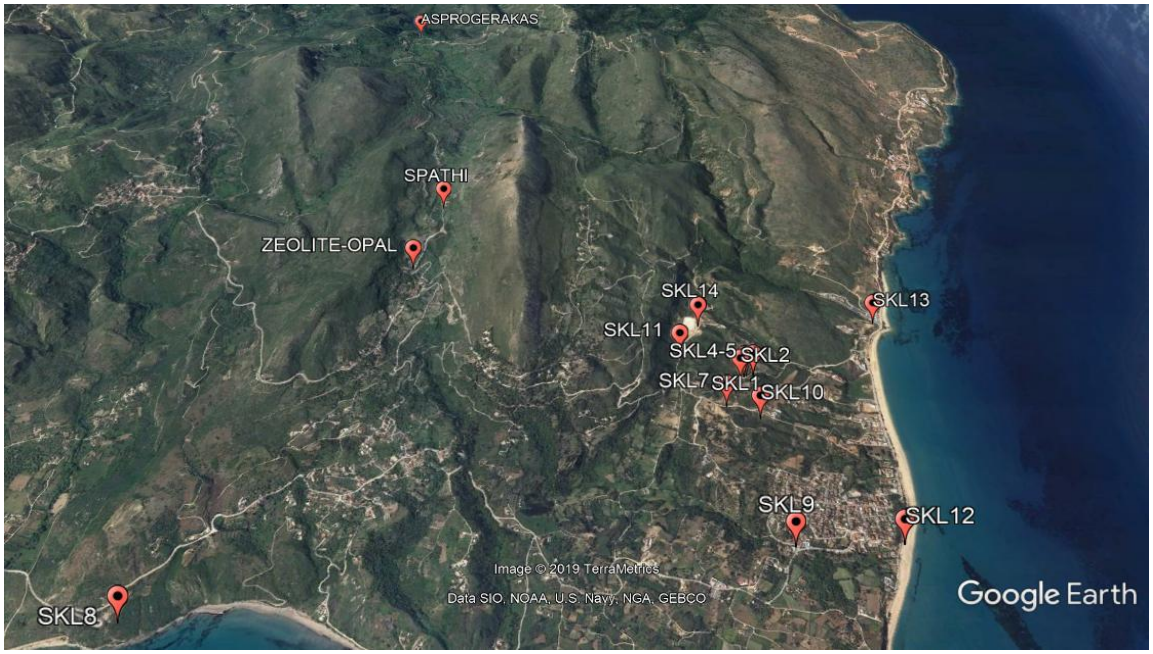
Silica sand is known as proppant or frac sand. It is pumped down holes, used in deep applications making the slits of the rocks wider and thus increasing the flow of natural gas or oil. Silica's hardness and durability provide a crush resistance of high pressures in more than 2,450 meters deep. In that kind of application, totally grain deposits are preferred, to increase the permeability to the maximum and to prevent the area from adverse intrusions. Additionally, the chemical purity that silica has is high to avoid chemical deterioration during corrosion events (Kamar, 2004).

3. STUDY AREA

The main area of study was Skala region, in Kefalonia island that had been extracted for silica sand during the past. It is located at the southern-east part of the island and a big part of the deposits near the coast has been extracted. There are two main quarries having a small distance in between and a difference of 20 meters altitude. The first extraction is 50m higher from the sea level and the second one is about 70m higher. The already extracted area is about 4 km² and the exploited material was around 20.000 m³.

PICTURE 1. Satellite Map of the quarrying area.

The whole region surround the quarries was examined for its geography and geomorphology, as well as its petrography in order to figure out the source of the material and the transition mode that provides these amounts of silica sand at the coast. The main source of the material is in Asprogerakas area, where there is a big formation of limestone with silica tubers. As the water flows from Asprogerakas mountain it sweeps along the carbonate material. Through the water transportation most of the carbonate material desolates, but the silica tubers that are included in the limestones are more durable, so they are not destroyed at all until they reach the coastal area. As a result, there is a remarkable amount of silica sand concentrated at Skala region. As we get closer to the coast we can observe that the material is finer grained than this one placed at higher altitudes, in which silica tubers dominate. The following map shows the whole study area and the places where the samples were collected.



PICTURE 2. Satellite Map of the explored area with the places where the samples were collected.

3.1 Geography and Geomorphology

Kefallinia is an island located in the Ionian Sea in Western Greece and it is expanded in a 781 km² area. It is notably a mountainous island with its highest mountain Ainos being 1,628 meters high. Ainos has a direction from NW to SE where it is expanded. Alongside eastward to the highest mountain there is a lower mountain chain.

Between the two mountains there is a groove that ends up at Poros valley and Arkalios plain in the south part of the island (Karymbalis et.al, 2012). The island has also two big peninsulas, one called Erissos in the north section and another one which is Paliki in the west. There are little gulfs in number, two of them are in the NE part of the island that is called Sami and Antisami gulfs. There is Mirtos gulf in NW side and one of the safest gulfs of Mediterranean Sea is this one in Argostoli, located in the west side of the island. The coasts are high and cragged but there are also areas in the west where sand dunes with fine-grained sand are expanded. There are a lot of faults in the west coasts of the island that limit the continental shelf of Greece. Due to these faults there are steep differences in the depth close to the coasts (Stefanatou and Triandi, 2009). There is no surface hydrographic network, but there are a lot of underground sources of water such as Koutavos, Karavomilos, Livadi and more that have a big water supply. The limestones that dominate the island allow the underground circulation of the water (Stefanatou and Triandi, 2009).

3.2 Climate

The climate in Kefallinia is temperate, characterized by mild winters and cool summers. The lowest temperature that has ever been observed is -3°C in Argostoli and the highest temperatures, up to 40°C, are observed only at the inner part of the island at closed areas. During autumn the temperature is usually higher than spring due to the warm winds that occur this season. The average temperature of the year is 15.6°C. The coldest period is in January and the warmest in August. In the cold season the humidity increases because of liquid winds that are produced in the southern part of Greece from September until May (Karymbalis et.al, 2012).

Glaciers are not a common phenomenon in Kefallinia, they have occurred sometimes only during winter period, but they are not expanded in a wide region, only spatially (Karymbalis et.al, 2012).

The island is characterized by more cloudless days (167 days yearly) than cloudy days (55 days yearly). As a result, Kefallinia is one of the sunniest areas of the country. The water precipitation is common due to the wet winds that move from the west to the east, during winter period. The highest limit of rain appears in December and the least in July. Hail fall in Kefallinia is more common than in other places especially during December and January (Karymbalis et.al, 2012).

3.3 Geology

3.3.1 Introduction

Greece is divided in different sections according to the type of sedimentation, the metamorphism and the tectonic context. Kefallinia Island belongs to Ionian and Paxoi zone that is the outer of all on which the Ionian zone lays. It derives from the western margin of the outer platform of Greece. Kefallinia is the place where we can see the biggest development of Paxoi zone, which is characterized by lats' domination that states the area of a margin (declination). The boundary of the zone to the North is not clear and to the West there is a subduction zone with volcanic formation, clastic material and evaporites. It is a shallow carbonate sedimentation with little double-unconformities during Paleogene that started from Upper Jurassic (it does not appear in Kefallinia) and was completed until Lower Miocene. Classic flysch is missing; however there is another deposition similar to it that is compounded of clay and marls. Tectonism in Paxoi zone occurred between Miocene and Pliocene, as well as in Kefallinia, but it has been continued at the present. The overthrust of the Ionian zone on Paxoi is observable form west Lefkada to east Kefallinia. In Kefallinia there are two smaller tectonic sections which are separated by an upthrust in between. One is Paliki section at the west part, which is a shallower platform than the this one of Ainos that is a slap platform. The upthrust of the two platforms passes through Argostoli gulf and it is seismic active (Papanikolaou, 1986).

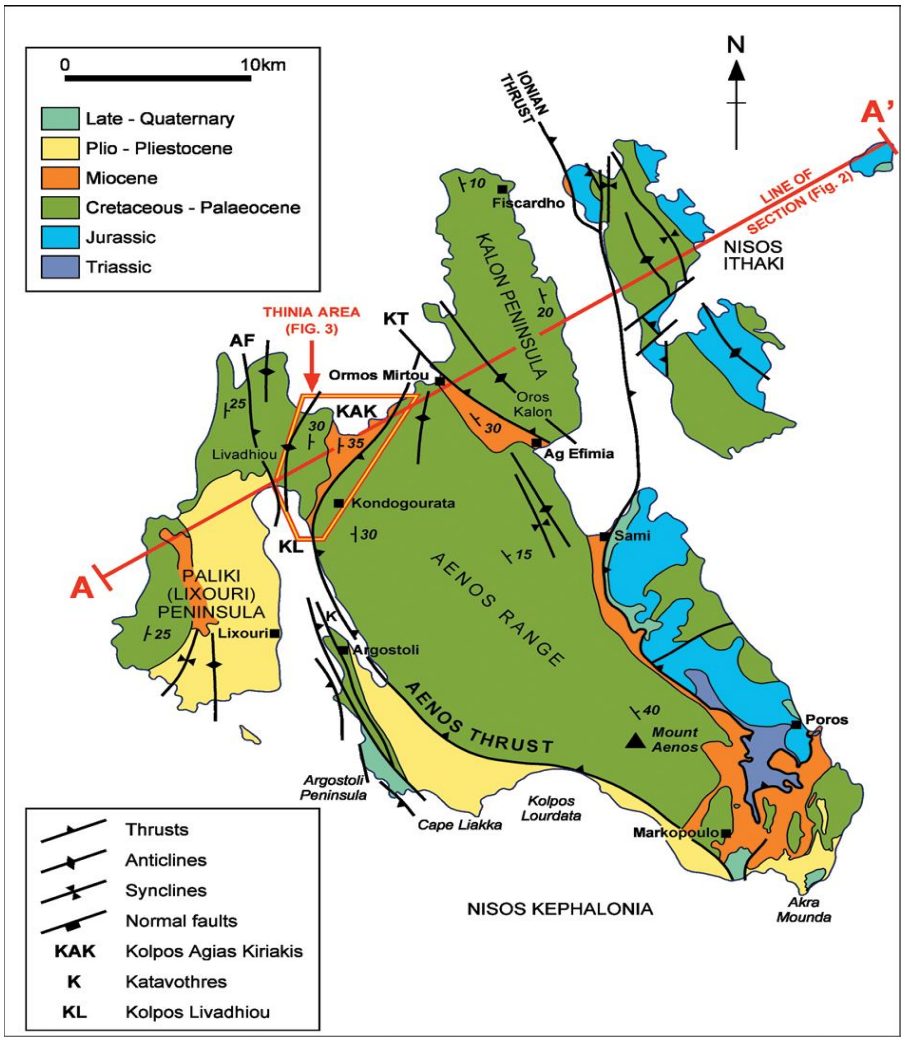


FIGURE 3. Geological Map of Kefallinia (Underhill, 1989).

3.3.2 Geological Setting

The sedimentation phases of the carbonate section differ during Cretaceous, but it is regularized during Quaternary (Lekkas et.al, 2001).

At the Peninsula of Paliki and Argostoli there is a shallow marine platform of white layered limestones, dolomitic limestones, corroded dolomites and uplifts of bioclastic coral limestones. The sequence of the sediments has been calculated up to 1000 meters for the Upper Cretaceous (Lekkas et.al, 2001).

In the central part of the Island there also shallow marine phases, however there are deeper phases that show the margin of a long-live cretaceous platform. There are shallow marine limestones, bioclastic and micritic limestones followed by micritic dolomitic limestones with bioclastic material (roudists and gastropods) (Lekkas et.al, 2001).

At the Peninsula of Erisos and Kalou at the northwest part of Kefallinia, the sedimentation phase responds to a margin where there is a slop area and the bottom of a basin. The sedimentation is more pelagic with a thickness of more than 1000 meters. The sequence involves layers of dolomites, limestones and flints (Lekkas et.al, 2001).

The clastic- clay-flysch sequence follows the carbonate sedimentation and it is up to 100 meters thick. Marl, sandstone, clay and conglomerate form this sequence, which has been observed only in Paliki, Argostoli and Kateleio (Lekkas et.al, 2001).

3.3.3 Tectonism

The tectonic structure of Kefallinia Island is the consequence of decompression gravitational influence of successive compressive deformations that happened per periods. There have been observed inversed faults that cut resent formations (Middle-Upper Pleistocene) at Argostoli Peninsula. Faults and upthrusts with slide lines appear to have horizontal and vertical component. There are also faults at Argostoli Peninsula and at the south-east part of the island with horizontal slide lines that do not move in long distances. Additionally, the existing regular faults, which have been observed at the tectonic draft of Arginia have its tectonic slide lines at a declined rift surface (Lekkas et.al, 2001).

According to geometric and kinematic details of the tectonic structure, we can describe the stages of the tectonic evolution of Kefallinia Island. The first stage took place during the Lower Pliocene when Ionian zone was placed on Paxoi zone. The intensive compression ended up to islands emergence and at the same time to folds creation. The first stage is followed by a decompression period during the Upper Pliocene-Lower Pleistocene. However, the compressive content continues acting deeper in the crust. The surface's lift and the gravitational force drive to the activation of big rift surfaces resulting to the formation of tectonic horns, such as Ainos mountain and basins. After the Lower Pleistocene, compression starts again activating new rift zones and new inversed faults are born, especially at Agrostoli Peninsula. Then follows the last stage and like in the second one, decompression takes place on the surface when deeper prevails compression, resulting to uplift and fault creation (Lekkas et.al, 2001).

4. MATERIALS AND METHODS

The fieldwork in Kefallinia Island took place in December and it lasted for three days from 17/12/2018 to 19/12/2018, in which the whole area around the main exploitation at Skala region was explored. The area of Skala belongs to the Ionian zone. The sample collection was started from the quarry area at Skala at a low altitude (50m) and it was continued examining the expansion and the origin of the onshore material. After the fieldwork the samples were taken for X-Ray, stereoscope analysis, carbonate free fraction and sieve analysis. The research took place to calculate the SiO_2 content of the collected material and to decide its most efficient use in construction according to composition and texture.

4.1 Sampling

The first samples were taken from the bed of a stream in the quarries area. Considering this sample as the lowest layer of the sedimentary column, the sample collection continued picking silica sand from the banking of the extraction higher from the ground. Samples were also collected from the second major area of extraction some meters higher from the first quarry. Also, many samples were taken from the surrounding area of the extractions and others were collected from places very close to the beach and on the beach. A number of fossils, such as shells, roots and animals' tooth were involved in the sediments. The findings confirmed the environment and the conditions of the sedimentation, as well as the age of the sediments. The two main quarries, where the samples SKL1, SKL2, SKL4-5 and SKL11, were collected are presented in the following photos.

First Quarry

PICTURE 3. The picture shows the banking of the extraction which was placed 50m from the coast. The sample SKL2 was collected from the banking of this extraction. The inclination of the layers is SE (38º4”53”B20º47’32”A).

PICTURE 4 . The picture shows the bed of a stream in the quarry. The sample SKL1 was taken from the ground of the extraction. (38º4’54”B20º47’33”A)

Second Quarry

PICTURE 5. The picture shows the banking of another extraction area, placed 70m from the coast. The samples SKL14 and SKL15 were collected from different stratigraphic levels of the quart beds. (38º4’44”B20º47’35”A)

PICTURE 6. The picture shows the actual position where the sample SKL11 was collected. (38º4’59”B20º47’19”A)

4.1.1 Macroscopic Description of the samples

- The samples SKL1, SKL2, SKL3, SKL4-5 were taken from the area of the first quarry at the altitude of 50m.
- SKL1 was observed to be a fine-grained material.
- SKL2 was also observed to be fine-grained, contains of big angular lats.
- SKL3 include of rounded silica residues, until 10 cm in length.
- SKL4-5 was characterized as Turbidite material with of coarse- and fine-grained alterations. It contains of small fossilized shells such as Ostrea, Balanus and Chlamys.
- The sand of SKL6 sample was observed to have no granulometry.
- SKL7 was taken from an area 10 meters higher than the first quarry, at the altitude of 70m. The material was taken from a solidify carbonate reddish formation.
- SKL8 was collected from an area between Skala and Kato Katelios, where there are the borders of the silica sand formation and the carbonate formation. The sand was observed to be fine grained and compact, rich in different sizes of fossils, especially dominated by Pecten.
- SKL9 was taken from a fine grained not layered formation at Skala area.
- The samples SKL10 and SKL11 were collected from the second big area of extraction.
- SKL10 consists of silica fractions and rabbits until 10 cm in length. It was observed that the recent pieces are not fine-grained, which shows a more dynamic environment.
- SKL11 was collected from a section of old-soil with sand bedrock, where a meteoric water circulation can be observed.
- SKL12 was taken from the sandy part of the beach at zero level.
- SKL13 was collected from an area next to the beach very rich in different types and species of fossils (bones, teeth, shells and roots). The sand material appears to be a turbiditic deposition in parts followed by thin clay layers of 30 cm thickness.

4.2. X-RAY Diffraction (XRD)

Sample SKL1

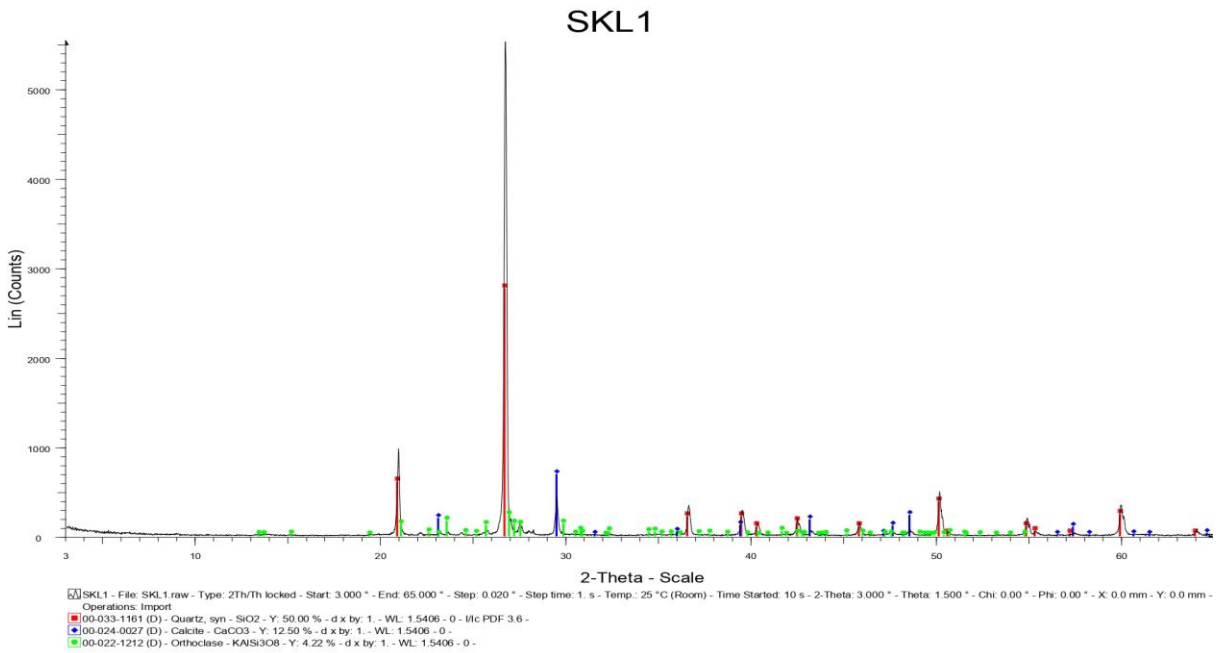


FIGURE 4. Mineral Analysis of the Sample SKL1 with XRD.

Sample SKL2

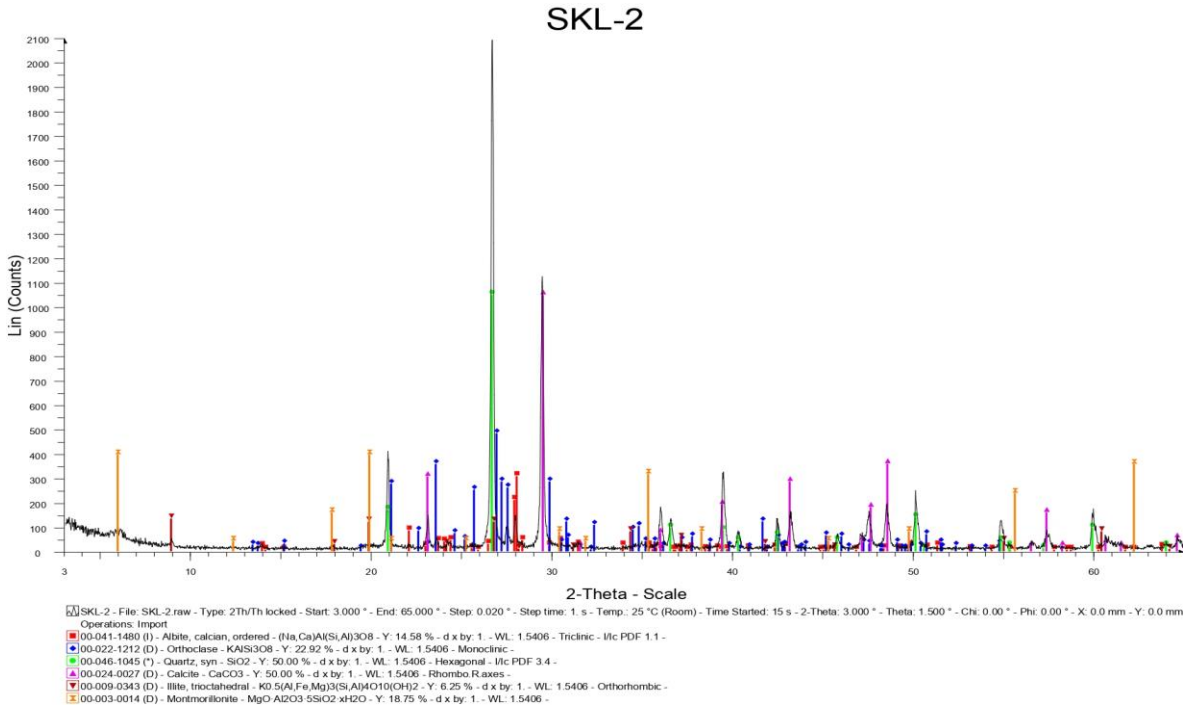


FIGURE 5. Mineral Analysis of the Sample SKL2 with XRD.

Sample SKL4

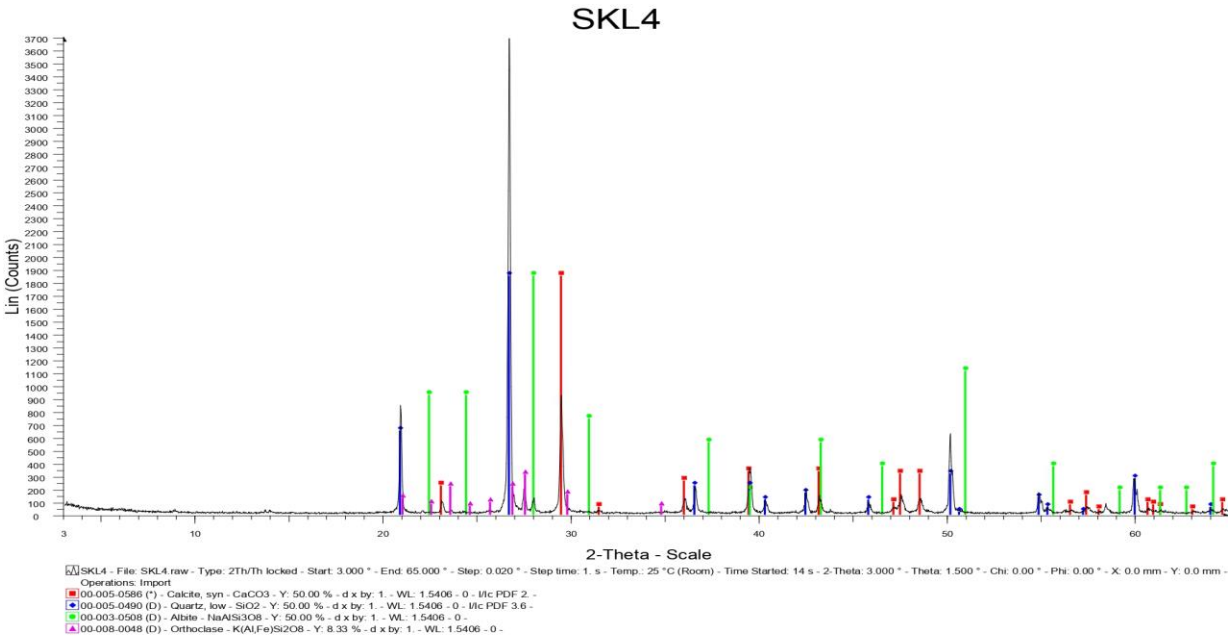


FIGURE 6. Mineral Analysis of the Sample SKL4 with XRD.

Sample SKL11

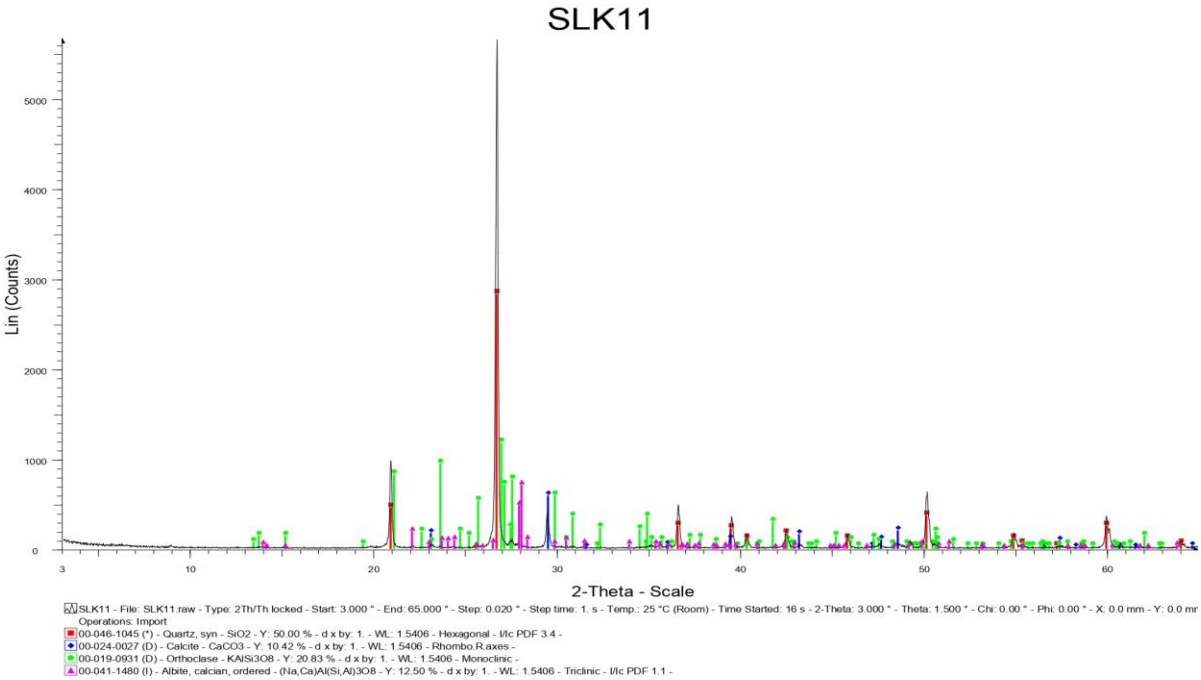


FIGURE 7. Mineral Analysis of the Sample SKL11 with XRD.

Sample SKL14

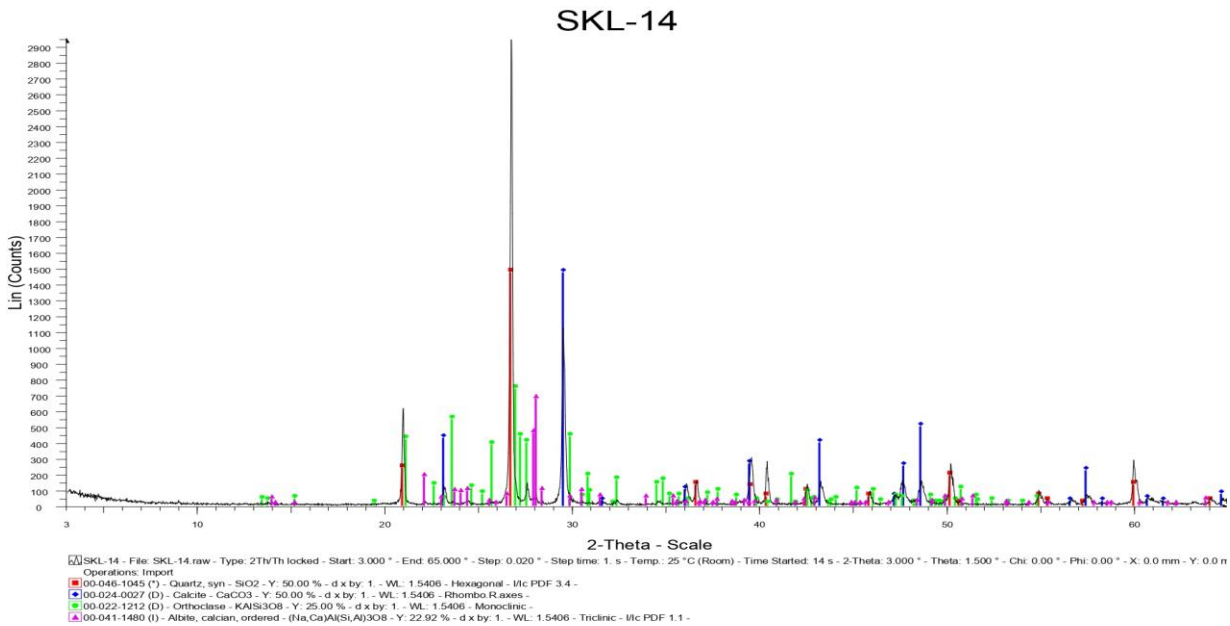


FIGURE 8. Mineral Analysis of the Sample SKL14 with XRD.

Sample SKL15

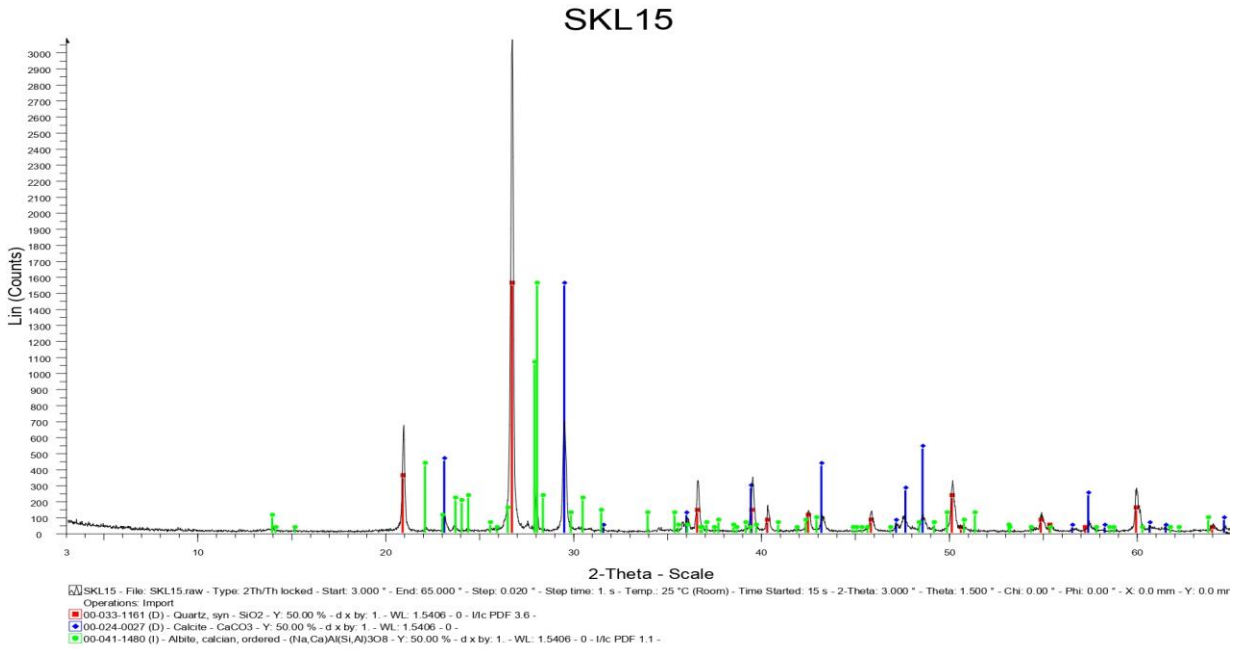


FIGURE 9. Mineral Analysis of the Sample SKL15 with XRD.

XRD Mineralogical Analysis of the Samples

Sample	Qtz	Cc	ill	feld
SKL1	MJ	MD	-	TR
SKL2	MJ	MJ	TR	TR
SKL4	MJ	MJ	-	TR
SKL11	MJ	MD	-	TR
SKL14	MJ	MJ	-	TR
SKL15	MJ	MD	-	TR

TABLE 1. Mineral analysis of the samples (XRD). **Qtz:** quartz, **Cc:** calcite, **ill:** Illite, **feld:** feldspar **MJ:** major mineral component, **MD:** medium mineral component, **TR:** trace mineral component.

4.3 Carbonate Free Fraction

The purity in silica of the material depends on the contaminants in other minerals such as calcite that worsen its quality. To examine the clarity of the material in SiO_2, $CaCO_3$ content had to be removed from the samples. Thus, all the samples were measured at high accuracy weight scale before and after $CaCO_3$ removal. 100mL of HCl 10% was used for all the samples. The HCl solution was added to the samples and they were left for seven days in order $CaCO_3$ to effervesce completely and to evaporate. The final $CaCO_3$ proportion is presented at the following Carbonate Free Fraction result table.

Sample	Initial Weight (gr)	HCl (mL)	Final Weight (gr)	$CaCO_3$ (gr)	$CaCO_3$ (%)
SKL1	10.10	30	8.02	2.08	**20.59**
SKL2	10.15	40	6.83	3.32	**32.71**
SKL4	10.08	44.5	7.52	2.56	**25.40**
SKL11	10.06	30	9.40	0.66	**6.56**
SKL14	10.07	30	7.32	2.75	**27.31**
SKL15	10.08	30	7.93	2.15	**21.33**

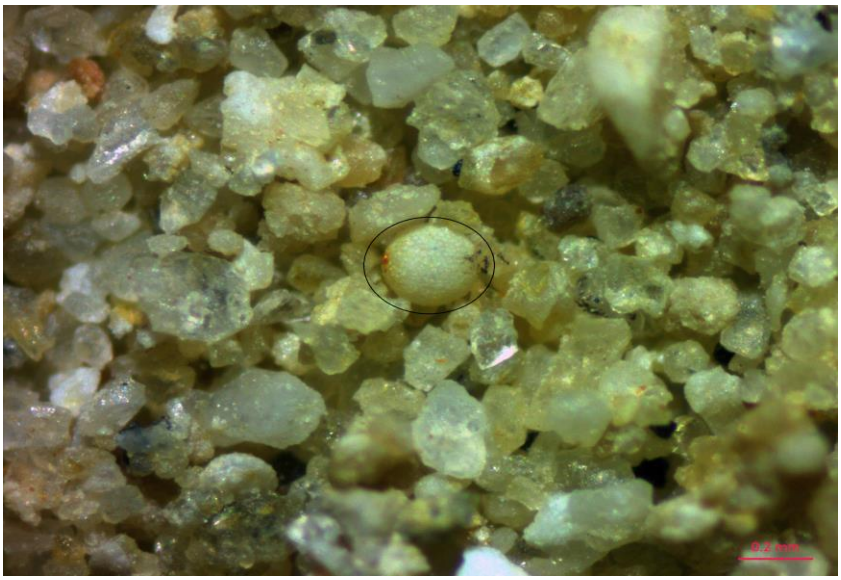
TABLE 2. Carbonate Free Fraction.

The carbonate content in the samples ranges from 6.56% to 32.71%. As the samples were collected from different outcrops and stratigraphic levels the $CaCO_3$-SiO_2 proportion varies considerably. The sample that has the lowest content in $CaCO_3$ is SKL11, which means it has better quality, dominated mostly by quartz.

4.4 Stereoscope Analysis

Sample SKL1

PICTURE 7. At the stereoscope picture there is a biogenic carbonate shell and small crystals of calcite and quartz. The major mineral component is quartz and the texture of its crystals is angular to sub-angular. In the middle of the picture there are femic impurities.

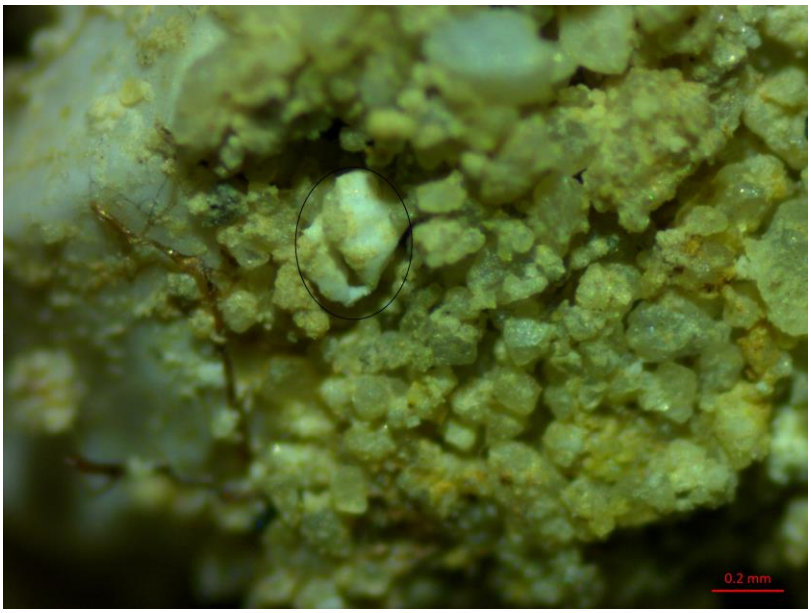


PICTURE 8. At the stereoscope picture there are mixed crystals of quartz, calcite and femic components and impurities. In the middle of the picture we can observe a biogenic fossil, recognized as Orbulina which belongs to Globigerinidae family.

Sample SKL2

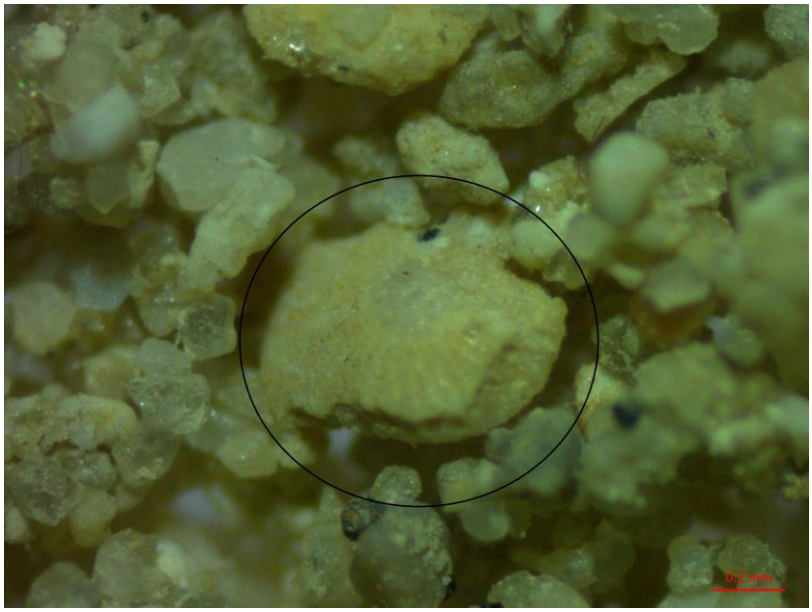
PICTURE 9. At the stereoscope picture there are clay minerals that coat the silica and carbonate material. The material is dominated by roots and impurities. In the middle of the picture we can observe a feldspar crystal.

PICTURE 10. At the stereoscope picture there are crystal and non-crystal aggregates mixed with biogenic carbonate remains. A chemical alteration is also visible at the middle-right part of the picture.



PICTURE 11. At the stereoscope picture we can observe that the sample is not pure in silica. It consists if roots, clay minerals and carbonate biogenic material.

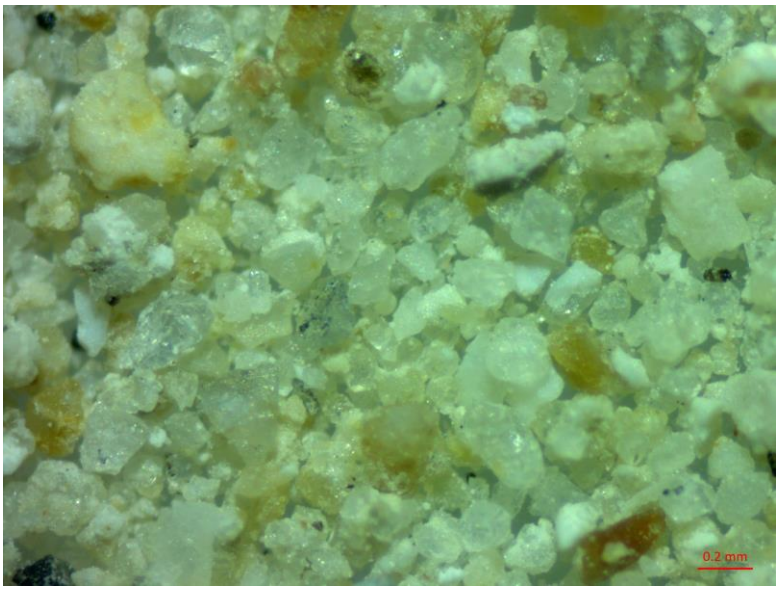
Sample SKL4



PICTURE 12. The stereoscope picture shows mixed quartz and calcite crystals of different size shaped angular to sub-angular. In the middle of the picture there is biogenic carbonate fossil.

PICTURE 13. The stereoscope picture shows granules of calcite and quartz, roots and femic minerals. The crystals are not so clean, as there are attached clay minerals and biogenic material on them.

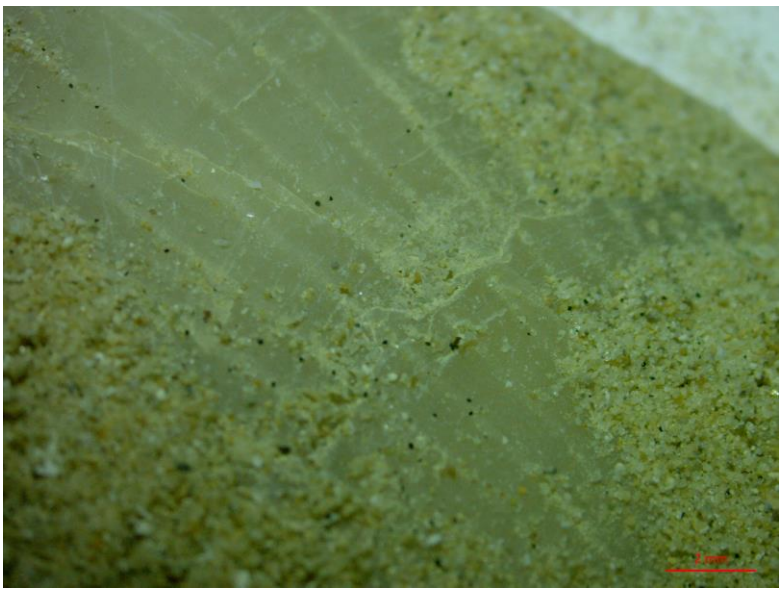
Sample SKL11



PICTURE 14. At the stereoscope picture we can observe that the sample is mainly dominated by in quartz. The crystals have angular to sub-angular shape.

PICTURE 15. The sample is rich in quartz. In the middle of the picture there is biogenic material.

Sample SKL14

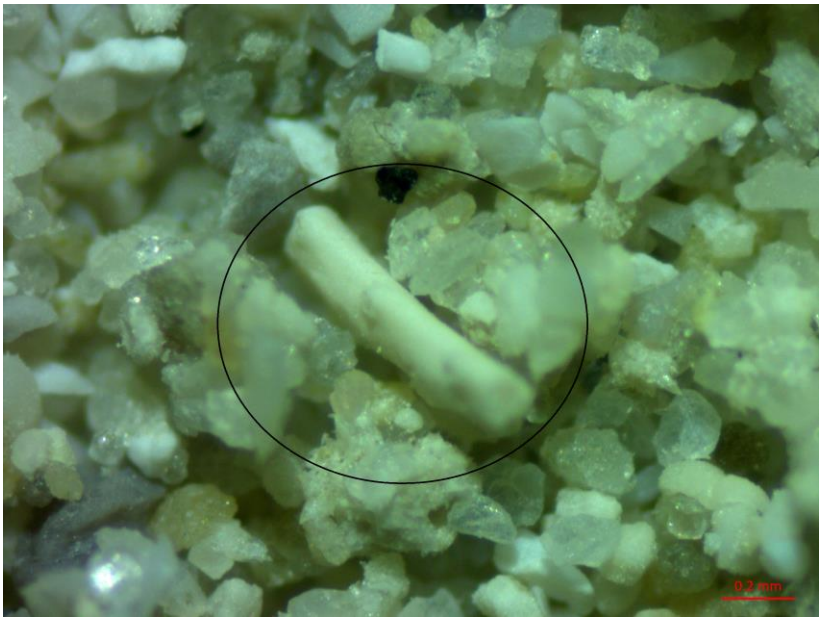


PICTURE 16. At the stereoscope picture there is an Ostrea shell, contained in the sample of the sand. The lines of the shell are very observable.

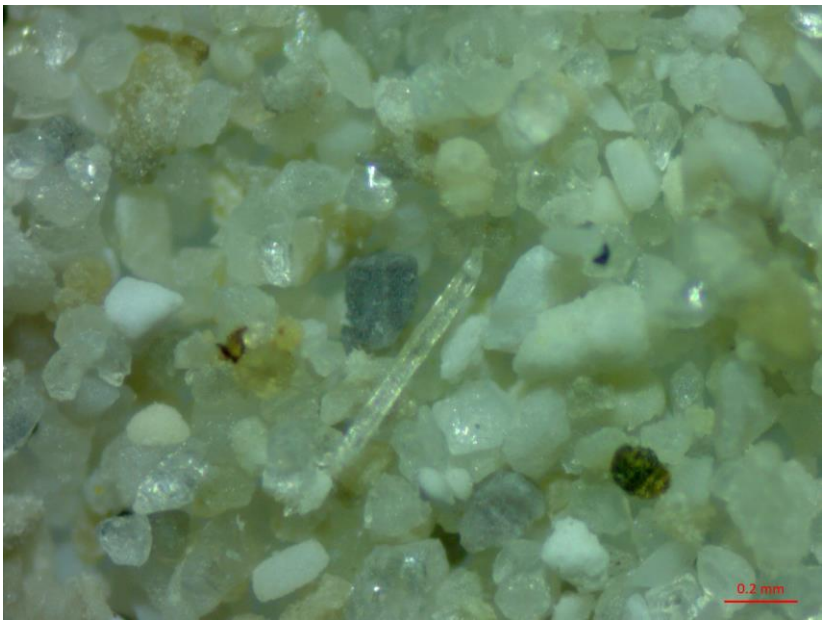
PICTURE 17. At the stereoscope picture there is a carbonate shell among silica and carbonate grains. The size of the grains differs, there are grain accumulations and femic and heavy minerals.

PICTURE 18. At the stereoscope picture the sample seem to be mostly siliceous with some biogenic carbonate material, such as the circled one.

Sample SKL15



PICTURE 19. The sample is rich in quartz crystals mostly angular, there is some biogenic carbonate material and some impurities.



PICTURE 20. The sample is mostly siliceous with big crystals of quartz. The mat-white crystals are calcific.

4.5 Sieve Analysis

Sample Statistics

The following table and graph (TABLE 3, GRAPH 7) present the proportion of sand, mud and gravel in each sample. The amount of sand in the samples varies from 81.3% to 98,2%. The samples that are dominated mostly by mud, consist of a low level of gravel.

	Percent (%)		
Sample	GRAVEL 4>x>2 mm	SAND 2>x>0.063 mm	MUD 0.063>x>0.001 mm
SKL1	0.0	**92.8**	7.2
SKL2	0.8	**87.1**	12.1
SKL4	15.8	**81.3**	3.0
SKL11	0.0	**84.4**	15.6
SKL14	0.1	**98.2**	1.8
SKL15	15.3	**83.7**	1.1

TABLE 3. Gravel, Sand and Mud proportions.

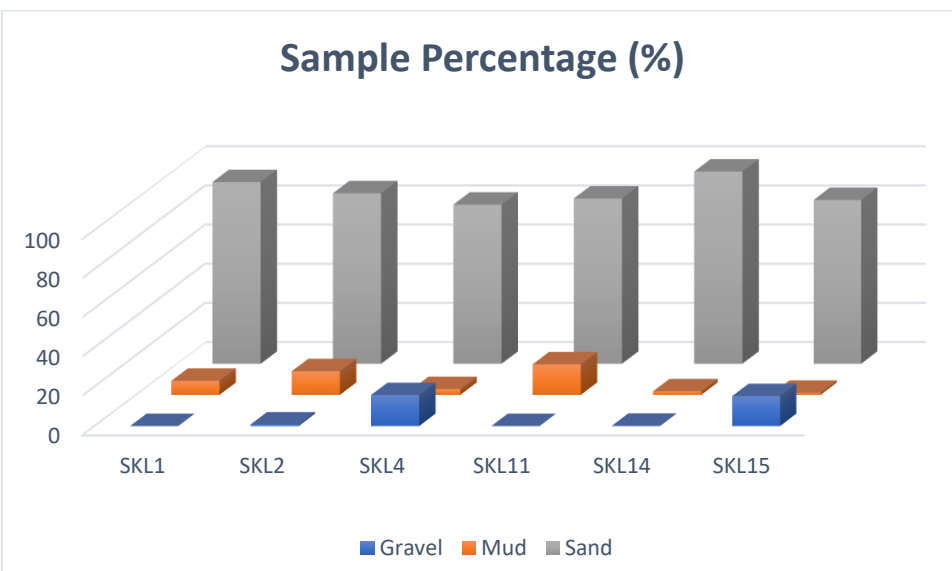


FIGURE 10. Samples percentages in gravel, sand and mud.

The following table (TABLE 4) refers to the Textural Group of the samples according to the quantity of sand, mud and gravel that each sample involves.

Sample	TEXTURAL GROUP
SKL1	Sand
SKL2	Slightly Gravelly Muddy Sand
SKL4	Medium Gravelly Fine Sand
SKL11	Muddy Sand
SKL14	Slightly Very Fine Gravelly Fine Sand
SKL15	Medium Gravelly Fine Sand

TABLE 4. Textural Group of the samples.

Folk and Ward Method Description

The following table (TABLE 5) shows the classification of the sand. Most of the samples are poorly to very poorly sorted apart from SKL1 and SKL14 that are moderately sorted.

Sample	MEAN	SORTING	SKEWNESS	KURTOSIS
SKL1	Very Fine Sand	Moderately Sorted	Symmetrical	Leptokurtic
SKL2	Fine Sand	Poorly Sorted	Coarse Skewed	Mesokurtic
SKL4	Medium Sand	Very Poorly Sorted	Very Coarse Skewed	Very Leptokurtic
SKL11	Very Fine Sand	Poorly Sorted	Symmetrical	Leptokurtic
SKL14	Fine Sand	Moderately Sorted	Coarse Skewed	Leptokurtic
SKL15	Fine Sand	Poorly Sorted	Very Coarse Skewed	Very Leptokurtic

TABLE 5. Folk and Ward Method Description.

5. RESULTS AND DISCUSSION

Fossils Results and Paleo-Environment

The shells that were found in the sediments belong to Pectinidae and Ostreidae families. The species were recognized as Flabelipecten and Chlamys. These fossils are purely sea-fossils that live in 50-meter depth and they are dated to Pliocene. The sedimentary sequence near the coast shows a high-energy environment in which among the shells, roots and animal's tooths was also found. The tooth was recognized as a lower m3 of a young Cervid, possibly a Dama dama, which is aged in Upper Pleistocene.

PICTURE 21. Cervid tooths fossil found in the sediments. (38°4'21"B20°47'47"A)

The carbonate sedimentation took place before silica material came at the area. It is supposed that water currents transported shells from deeper sea environment to shallower environment, closer to the coast, where they were mixed with silica and carbonate pebbles, transported from the mountain. The paleo-environment of the area of study seems to be a coastal environment with transported, reworked marine material. The disturbance of the area started possibly in Pliocene and lasted until Pleistocene, when the silica material in chert form, was transported and deposited, at a deltaic environment.

Source of the Silica Material

The silica material is placed on sediments dated in Pliocene, which confirms its formation after it, during Pleistocene. The silica material derives from cherts that are included in Mesozoic limestone at the back side of Asprogerakas mountain. Because the limestone is an easily eroded type of rock the more durable silica material, included in the mother rock, started transporting in the Upper Pleistocene through erosion and corrosion processes without breaking down.

The different influence of the water on SiO_2 and $CaCO_3$ is the main reason for the silica domination in the area, despite the fact that the mother rock of the place has carbonate composition. The calcite is usually dissolute by water, get involved in it and transported with it. On the other hand, silica is not dissolved by water it, therefore, remains its initial composition and characteristics. This is the most possible explanation for the appearance of high-purity silica sand on a carbonate basement.

Quality of the Silica Material

According to the Carbonate Free Fraction Analysis, $CaCO_3$ content varies from 6,5% to 32%, which means that the purity in SiO_2, of the sand in Skala area, varies from 93,5% to 68%. Additionally, the sand material is characterized by heterogeneity. It is a mixture of marine and terrestrial products, since it was deposited by river's estuary, which does not display a mild deposition environment. The material appears with alterations of very fine-grained sand and not fine-grained sand. Comparing the results of X-Ray Diffraction and Carbonate Free Fraction Analysis with those of Sieve Analysis, it seems that samples with high SiO_2 content are not as fine-sorted as others with lower SiO_2 content. As we get closer to the sea silica sand consists of materials that deteriorate its quality such as silt and clay. The moderate quality of the silica sand is a possible reason that the cement companies stopped exploiting the area.

Suggested uses for the Silica Material

The quality of the silica sand is moderately good, but not high. It means that it cannot be used as the main component in any application, although it was used as raw material in clinker production which is the main component of cement. The silica sand at Skala region in Kefallinia Island can be used as adjunct material in specific mortars to improve its quality and durability. Adding a desirable proportion of SiO_2 in the carbonate/silica natural mixture of Skala raw material, it can be provided a better silica-rich construction product due to its physical and chemical properties.

Another use which is relevant with the touristic activity in the island and neighboring Zakynthos Island is its application in beaches which suffer from erosion phenomena, as replenishment material. One of the most important criteria for choosing the replenishment material is the chemical and physical relation with the already existed sand on the beach. The silica sand formation at Skala does meet this criterion for being applicable at Kefallinia and Zakynthos Island as beaches renourish material. Moreover, the replenish material should be coarser than the eroding or with low fine contents, which is a fact for some of the collected samples. Additionally, the depletion of carbonate material and the necessity for beaches restoration, show that the only product that can contribute and improve the quality and safety of the beach without environmental consequences is silica or quartzose sand.

6. CONCLUSIONS

- The formation of Pleistocene silica sand on a Pliocene carbonate background can be explained through the source of the silica material from silica cherts laid between Mesozoic limestones at the back side of the mountain.

- The reason for more silica material remained at the coast than carbonate is because $CaCO_3$ is dissolved in the water and transported within it after erosion and corrosion of the mother carbonate rock. On the other hand, silica in chert form is durable, it is not dissolved in the water, and thus it is transported in short distances.

- The SiO_2 proportion in the silica sand varies from **93.5%** to 68.0%.

- The fact that the silica content varies in combination with shells, clay and other impurities involved in the silica material, automatically deteriorates its quality. Thus, a cleaning process of the silica sand, before it is used in any application, is necessary.

- The quality of the silica sand is not high; it is not a competitive raw material to other silica rich materials that are currently in use in Greece for the construction industries. However, the material could be extracted and used for the necessities of the local area, such as beach replenishment.

- Another reason that complicates the extraction of the material in huge amounts is that the present area is residential and touristic. The establishment of quarries and the exploitation will transform the area at a construction site, causing noise and pollution.

- The silica sand of Skala region in Kefallinia can be used as supplementary material in carbonate mortars, cement and concrete, increasing durability and quality. At the same time, it contributes to avoid the consumption of $CaCO_3$ and natural occurring aggregates that are decreased.

- Another suggested use of the silica material is in Beach Nourishment application. Its characteristics can support application in Kefallinia and Zakynthos Island, since the distances are small enough for the transportation of the material. Additionally, the material does not consist of heavy minerals and other undesirable components for a coastal environment. It only consists of low quantities of clay, which is easy removal through the cleaning process.

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