

Raman Spectroscopic Analysis of Common Minerals in Sri Lanka

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Abstract

Sri Lanka is rich in high-purity minerals, and this mini-research project aims to analyze their Raman spectra. We used common minerals like Calcite, Dolomite, Apatite, Quartz, Feldspar, Graphite, and Mica. These minerals were grouped based on similar chemical and physical properties. For instance, Group 1 included Calcite, Dolomite, and Apatite, containing calcium compounds such as (CaCO_3) , $(\text{CaMg}(\text{CO}_3)_2)$, and $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$ respectively. Their Raman spectra identified vibration modes corresponding to $(\text{CO}_3)^{2-}$, $(\text{PO}_4)^{3-}$, and MgO bonds, with prominent peaks at 1075 cm^{-1} , 1099 cm^{-1} , and 962 cm^{-1} . Quartz varieties like crystal, milky, rose, and smokey quartz showed overlapping peaks around 465 cm^{-1} attributed to SiO_2 vibrations, with unique peaks observed around 1162 cm^{-1} . Feldspar samples, including Amazonite and an unknown variety, showed distinct peaks between 450 and 515 cm^{-1} due to AT_4O_8 structures with varying Si : Al ratios. Graphite's G band appeared at 1088 cm^{-1} , and Mica (Phlogopite) showed peaks at 187 cm^{-1} and 688 cm^{-1} , reflecting its MgO_6 trioctahedral structure and Si-O-Si bonds.

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1 Introduction

Raman spectroscopy is a non-destructive analytical technique widely used for identification and characteristics of materials. It provides vibrational fingerprints of chemical compounds. It is used to determine vibrational modes of molecules. This powerful technique can be used to analyse vibrational properties of solid, liquid and gaseous samples [1]. In Raman spectrometry, a laser beam is directed towards to a sample, and the scattered light is detected and analysed. This technique has been used to analysis of various materials including minerals. In this research project solid samples of minerals are used to analyse by Raman spectroscopy. This technique is based on the interaction of the laser light with the crystal lattice of the mineral, and it causes a change in the energy and wavelength of the scattered light. Information about the vibrational modes of the mineral is provided by the resulting Raman spectrum. This spectrum can be used to identify its composition.

Sri Lanka is enriched with many mineral varieties with high purity. Although Raman Spectroscopy is used to analyse various minerals, there is no data base created on Raman spectroscopy of Sri Lankan minerals. Purpose of this mini-research is to obtain Raman Spectrums of minerals in Sri Lanka and analyse them. Calcite [2], Dolomite, Apatite, Quartz [3] and Feldspar are studied and analysed in this research project. In order to do that, some of these minerals are divided into groups or categories and their Raman spectrums are analysed and compared. This categorization is based on composition and physical properties of the minerals. First group is consisting with Calcite, Dolomite and Appetite. They have Calcium based composition [4], which are calcium carbonate (CaCO_3), calcium magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$) and $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$ respectively. These minerals can be differentiated and characterized by the peak occurrence due to vibrational modes of $(\text{CO}_3)^{2-}$ and $(\text{PO}_4)^{3-}$. Second category is Quartz and four variety of quartz named as Cristal quartz, Milky quartz, Smoky quartz and Rose quartz are used to obtain their Raman spectrums. Si Lanakan Quartz known to be composed with 94% of SiO_2 purity. Their colour has been changed due to the impurities. Crystal quartz are almost pure SiO_2 , hence they are colourless or more crystal-alike. Milky quartz has its colour due to gas and fluids the inside inclusions or the presence of Ca. Reason for the colour of Rose and Smokey quarts are Mn and Al respectively. In this study, it was intended to find a method to differentiate those Quartz categories using the Raman spectroscopy. Feldspar are in the third group. Also Raman spectrums of Mica and Graphite were obtained and analysed individually.

Overall, Raman spectroscopy is a valuable tool in mineral analysis, providing information about the composition, structure, and properties of minerals in a rapid and non-destructive way.

2 Theory

2.1 Raman Spectroscopy

An effective method for identifying chemical species is Raman spectroscopy. Raman spectroscopy, like other spectroscopic methods, finds specific interactions of light with materials. This method specifically makes use of Stokes and Anti-Stokes scattering to look at molecule structure. There are several forms of scattering that can happen when light from the visible or near infrared (NIR) ranges interacts with a molecule.

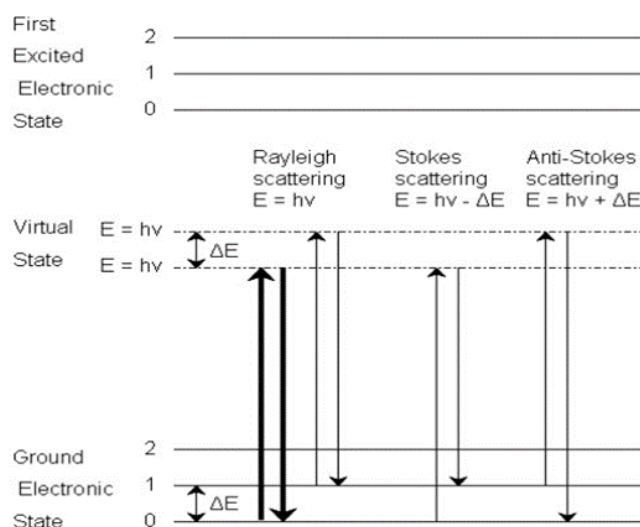


Figure 1: Three types of scattering by a molecule excited by a photon with energy $E = h\nu$. The most common transition is marked with bold arrows.

An incident photon with energy $h\nu$ lifts the molecule from a vibrational state to one of the many virtual states that are situated between the ground and first electronic states in all three forms of scattering. The manner in which the molecule relaxes following stimulation determines the type of scattering that is seen.

2.1.1 Rayleigh Scattering

1. The molecule is excited to any virtual state.
2. The molecule relaxes back to its original state.
3. The photon is scattered elastically, leaving with its original energy.

2.1.2 Stokes Scattering

1. The molecule is excited to any virtual state.
2. The molecule relaxes back to a higher vibrational state than it had originally.
3. The photon leaves with energy $h\nu - \Delta E$ and has been scattered inelastically.

2.1.3 Anti-Stokes Scattering

1. The molecule begins in a vibrationally excited state.
2. The molecule is excited to any virtual state.
3. The molecule relaxes back to a lower vibrational state than it had originally.
4. The photon leaves with energy $h\nu + \Delta E$, and has been scattered superelastically.

Since there is no requirement for the molecule's vibrational state to change, Rayleigh scattering is by far the most frequent transition. The least frequent transition is the anti-Stokes transition because a vibrationally excited state of the molecule must exist before the photon impacted upon it. Raman measurements often only employ Stokes scattering due to the weak anti-Stokes signal and the need for filters that exclude photons with incident energy and above.

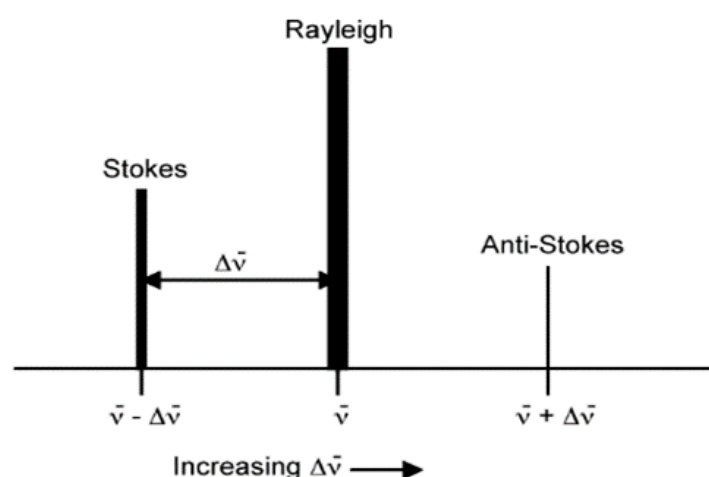


Figure 2: Location and relative intensity (indicated by peak height and width) of the Stokes and anti-Stokes scattering relative to Rayleigh scattering

The Stokes and anti-Stokes transitions' effect on the energy difference between incoming and scattered photons is measured using Raman spectroscopy. The change in wavenumber from the incident light source is commonly used to quantify this. Raman measurements may be made with sources of any wavelength because they measure the change in wavenumber; however, the near infrared and visible spectrum are often conducted. While ultraviolet photons could also be used, they often lead to the sample's photo-decomposition.

2.1.4 The G Band

The so-called G-band, which is normally visible at a wavelength of around 1600cm^{-1} , is made up of the tangential modes, which are the most intense high-energy modes of Single-Walled Carbon Nanotubes (SWNTs). Atomic displacements for this mode take happen in the circumferential direction. Independent of the RBM observation, spectra at this frequency can be employed for SWNT characterization. Although the data provided is less accurate than that of

the Radial Breathing Mode (RBM) feature, this multi-peak feature can be used, for instance, to characterize diameter and provides details about the metallic nature of the SWNTs in resonance with the laser line. The 2D honeycomb lattice's sp² bonds vibrate in plane, causing the G band to form. The G band may shift slightly to a higher wave number as a result of the addition of contaminants to the graphite.

2.1.5 Raman Spectroscopy

Raman spectroscopy is known to be a vibrational technique and it has an extreme sensitiveness to the geometric structure and the chemical bonds within a molecule. It is possible to define a Raman fingerprint for most of the molecules. This uniqueness of Raman spectra for any molecule is exploited to uncover lot of information about the observed molecule. This sensitivity to geometry and the bonding is the reason it produces different Raman spectra for different materials but with some major commonalities. It is possible to make accurate statements about the layer thickness, Oxidization levels and defects of Graphene based sample.

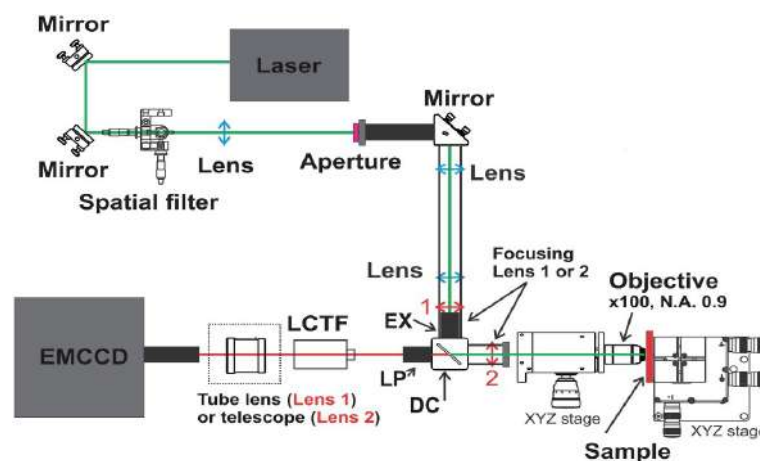


Figure 3: Location and relative intensity (Simple Block Diagram of a Raman spectrometer)

The laser generates photons at a certain wavelength, let's say 532 nm, and these photons pass through the dichroic mirror unaltered. The laser beam is then aimed at the sample while passing through the microscope's objective. The bulk of the scattered photons go back through the objective and reach the dichroic mirror when the laser beam scatters after striking the sample. The 532 nm photons are filtered at the dichroic mirror, while all other photons of a different wavelength can pass through and reach the spectrometer's lens.

This experiment has employed Raman Spectroscopy with 532 nm laser light. The Green color laser scatters as it strikes the material being viewed, sending back a large majority of the photons unchanged and relatively few altered photons. The photons are absorbed by the electrons in this situation, which then excite them to unstable energy levels known as virtual energy levels. Electrons would immediately de-excite because virtual levels are inherently unstable. Anti-Stokes scattering is a phenomenon that occurs during the de-excitation process in which

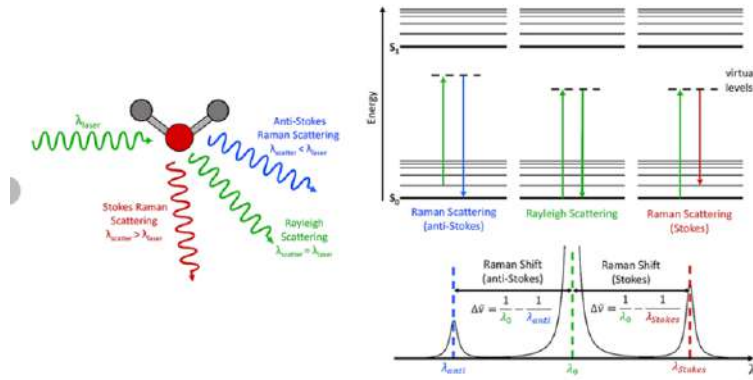


Figure 4: Energy diagrams of Raman Scattering

On top is the energy level diagram of the Rayleigh, stokes and anti-stokes scattering and lower diagram shows the approximated intensities of the three scattering modes

some stimulated electrons fall into lower energy levels than they did prior to the excitation. Another fraction of electrons would drop to a much higher energy level than they were before the excitation and this phenomenon known as stokes scattering. Both anti-stoke and stoke scattering are identified as Raman scattering and these energy differences of photons occur in vibrational energy levels.

In this study of minerals, the stokes scattering was given the sole consideration as all the expected peaks occur in lower energy region or at higher wavelengths relative to the laser. The equation for the Raman Shift is as follows,

$$\Delta V = \frac{1}{\lambda_0} - \frac{1}{\lambda}$$

2.2 Minerals

Minerals are those substances found in meals and in the ground that our bodies require for healthy growth and development. Natural homogeneous solid that is created by inorganic processes and has a clearly defined chemical composition and highly organized atomic organization. About 100 of the known mineral species—the so-called rock-forming minerals—make up the majority of the known mineral species, which number in the thousands. Mineral Identification.

Over 5800 different minerals exist. Each mineral is categorized according to both its crystal structure (the arrangement of the atoms when they lock together) and chemical makeup (the components from which it is made). Graphite and diamond are distinct minerals even though they both contain the same ingredient, carbon.

The physical characteristics of a mineral, such as color, hardness, density, or how it scatters or reflects light, are influenced by its distinct chemical makeup and crystal structure. These characteristics can be tested to identify unknown minerals. Complex tests like those involving magnetism, radioactivity, an acidic reaction, or x-rays are occasionally required. Although they may appear quite different, all minerals of the same species, like quartz, have the same x-ray

pattern. Classification and identification of minerals could be done according to :

- Weight and Density
- Magnetism
- Crystal Structure
- Colour and Streak
- Lustre
- Tenacity
- Cleavage and Fracture

Raman Spectroscopy is a powerful method used for characterization of materials. It provides vibrational fingerprints of chemical compounds. This technique has been used to analysis of various materials including minerals. Calcite, Quartz , Dolomite, Gypsum, Bassanite, Marble , Apatite, and Anhydrite are few of them. Sri Lanka is enriched with many mineral varieties with high purity. In order to do that samples of Graphite, Quartz, Marble, Apatite, Calcite and Dolomite from various places from Sri Lanka are intended to be used. Using Raman spectroscopy is advantageous since it is a non-destructive technique and more sensible for observing chemical bonds.

2.2.1 Calcite

CaCO_3 is the chemical formula of the mineral calcite, which forms rocks. It occurs often in igneous, metamorphic, and sedimentary rocks all throughout the world. The main component of marble and limestone is calcite. These rocks are quite prevalent and make up a sizable amount of the crust of the Earth. Calcite is one of the most often utilized minerals because of its characteristics. Construction materials, abrasives, agricultural soil treatment, aggregate for building, pigments, pharmaceuticals, and other uses are all included. Compared to other minerals, it is used more often.

2.2.2 Dolomite

A typical mineral that forms rocks is dolomite. Its chemical formula is $\text{CaMg}(\text{CO}_3)_2$, which indicates that it is a calcium magnesium carbonate. It is the main constituent of the metamorphic rock known as dolomitic marble as well as the sedimentary rock known as dolostone. Dolomite has three ideal cleavage directions. There are not many uses for dolomite as a mineral. Dolostone is most frequently used in the building sector. Dolomite is valuable because of how it reacts with acid. Magnesium (MgO) is found in dolomite, which is also used to make glass, bricks, and ceramics. It is also utilized as a sintering agent and flux in the manufacture of metals.

2.2.3 Apatite

The word "Apatite" refers to a collection of phosphate minerals having comparable chemical make-ups and physical characteristics. They are a crucial component of phosphorite, a rock that is mined for its phosphorus concentration and used to create chemicals, fertilizers, and acids. General formula of Apatite is $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$. The Mohs Hardness Scale's index mineral with a hardness of five, apatite, has a very constant hardness. Sometimes, specimens with exceptional color and clarity are cut into faceted jewels. Cut into cabochons are those with good color and translucence. Apatite often has a green color, although it also comes in yellow, brown, blue, purple, pink, and colorless varieties. The majority of the phosphate rock that is mined worldwide is used to make phosphate fertilizer. It is also used to produce animal feed supplements, phosphoric acid, elemental phosphorous, and phosphate compounds for the chemical industry.

2.2.4 Quartz

Quartz is one of the most common minerals in the Earth's crust. Quartz is a hard, crystalline mineral composed of silica (silicon dioxide). The atoms are linked in a continuous framework of SiO_4 silicon–oxygen tetrahedra, with each oxygen being shared between two tetrahedra, giving an overall chemical formula of SiO_2 . There are main varieties quartz :

- Crystal quartz
- Amethyst
- Blue quartz
- Dumortierite quartz
- Citrine
- Milky quartz
- Rose quartz
- Smoky quartz
- Prasiolite

2.2.5 Feldspar

Over 50% of the Earth's crust is made up of a large group of silicate minerals that form rocks known as feldspar. All around the world, they may be discovered in sedimentary, metamorphic, and igneous rocks. Feldspar minerals have a lot of the same structural, chemical, and physical characteristics. Amazonite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), Orthoclase (KAlSi_3O_8), Albite ($\text{NaAlSi}_3\text{O}_8$), and

Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) are examples of common feldspars. Even though there are several feldspar minerals, they all have a limited set of physical characteristics that are very uniform. The majority of them have two beautiful cleavage orientations that cross at or near 90 degrees. Most of this feldspar is crushed into fine powders or granules, which are then used in the production of items including plate glass, ceramic tile, fiberglass insulation, paints, plastics, ceramics, and container glass.

2.2.6 Amazonite

The mineral class of Microcline includes the variation of potassium feldspar known as amazonite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). It has a vitreous lustre and is a piece of the triclinic crystal system. There are purple, grey, green, and blue tones in amazonite. It often has a greenish blue hue. Amazonite is said to reduce stress and promote clarity. Amazonite is used to treat exhaustion, trauma, and other conditions that could sap a person's energy. Amazonite is thought to aid in the treatment of alcoholism as well as thyroid gland issues.

2.2.7 Graphite

A mineral made entirely of the element carbon is called graphite. Diamond, another pure carbon substance, and graphite have the same chemical makeup, although they have completely distinct molecular structures. Their physical traits are practically opposite as a result. Although graphite is a common mineral, fine crystals are uncommon. Large Graphite veins in the majority of mining regions generate massive amounts of the mineral, although collector examples in desirable crystal forms are uncommon. Graphite specimens should be handled with extreme caution due to their fragility, especially thin crystals. Crystals could be challenging to wash since they rapidly peel off and become destroyed. Graphite will smear on its surface as well. Much of the commercially mined Graphite is used for pencil fillings. The "lead" filling in pencils is in fact composed of a mixture of Graphite and clay. Graphite's main function, however, is as a lubricant. It has many electrical uses, primarily because it is the only common nonmetal that is a good conductor of electricity.

2.2.8 Mica

A set of minerals with comparable physical and chemical properties are referred to as mica. Since they all form in distinct layers, they are all silicate minerals known as sheet silicates. Micas are generally soft and light, and their sheets and flakes are adaptable. Mica is not an electrical conductor and is heat-resistant. Mica minerals come in 37 distinct varieties. The most prevalent ones include brown phlogopite, black biotite, purple lepidolite, and transparent muscovite. Grounded mica is primarily used in the joint compound for gypsum wallboard, where it serves as a filler and extender, enhances workability, and avoids cracking. Due to its low weight and platy shape, powdered mica is utilized in the paint industry as a pigment

extender that also helps with suspension. Additionally, the ground mica lessens checking and chalking, prevents shrinkage and shearing of the paint film, increases resistance to weathering and water penetration, and brightens the tone of colored pigments. Additionally, ground mica is added to drilling "muds" in the well-drilling sector.

The plastics industry employed ground mica as a reinforcing agent, extender, and filler. The production of moulded rubber goods, including tires, employs ground mica as an inert filler and a mould lubricant. The electronic and electrical sectors are the main users of sheet mica. The main applications for sheet and block mica include electrical insulators for electronic equipment, thermal insulation, gauge 'glass', windows for stove and kerosene heaters, dielectrics for capacitors, decorative panels for lamps and windows, insulation for electric motor and generator armatures, field coil insulation and insulation for magnet and commutator cores.

3 Methodology

3.1 The Raman Spectrometer

For this experiment Kymera 328i-A Adaptive Focus Imaging Spectrograph spectrometer by Andor was used to get the data of minerals.

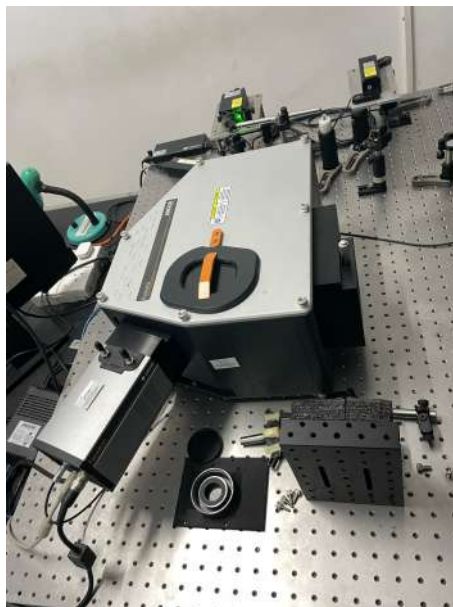


Figure 5: Kymera 328i-A Adaptive Focus Imaging Spectrograph spectrometer by Andor

3.2 Processing Mineral Samples

The samples were collected and all samples were at the solid state. A considerable space on the surface of each the samples were cut and polished [Figure 7]. This cutting and polishing process allowed to make an uniform surface on the each samples and it allowed to illuminate the surface of the sample without scattering with the laser.

3.3 Taking Raman Spectral Data of Samples

3.3.1 Initial setup of the Raman Spectrometer

Before collecting sample data, the spectrometer was calibrated by setting the grating to 1200. The spectrometer was then kept steady to reduce its inner operating temperature to -80 degrees Celsius. The sulphur sample was then placed on the sampling table. The 532 nm laser was then turned on, and the laser light's path was cleared to illuminate the sulphur sample. The laser focused the sample by moving the converging lens as needed. The computer was then turned on, and the SOLIS software was launched. The laser's power was measured using a power meter. The sulphur sample was set to single accumulations, and the exposure time was set to 5 seconds. The power meter was then placed directly in front of the laser light, and the power

was adjusted to 55 mW. The power meter was removed from the light path, and the required Raman spectral data was acquired by hitting the acquisition button on the software. In addition, the most prominent sulphur peaks were captured for the Raman shift calibration process.

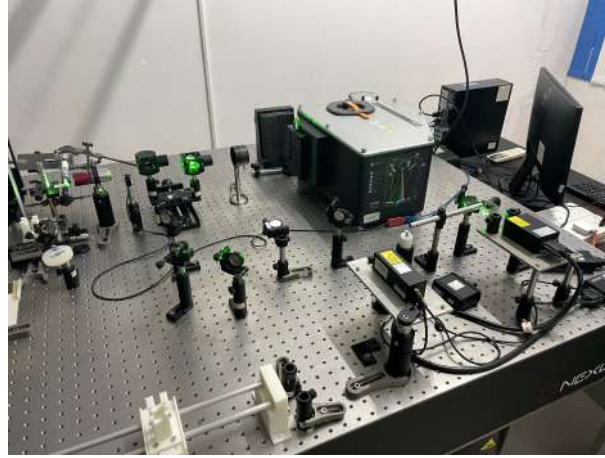


Figure 6: The experimental Setup. The spectrometer, laser and focusing lenses are showing.

3.3.2 The process of taking Raman spectra of samples

For the all samples, the grating of the spectrometer was kept as 1200. Other parameters were changed for each sample.



Figure 7: Minerals which were used for the experiment. (a):Feldspar (b):Milky Quartz (c):Crystal Quartz (d):Calcite (e):Apatite (f):Smokey Quartz (g):Amazonite (h):Dolomite (i):Graphite (j):Rose Quartz (k):Mica

For quartz family which are crystal quartz, milky quartz, rose quartz and smokey quartz the Raman data was gathered as follows. For the crystal quartz the number of accumulations were

set to 1 and the exposure time was set to 30 seconds. And the power of the laser was set as 100 mW. This settings was given the data set with minimum background noise. Then the collected data was recorded. The same procedure was followed and was taken the Raman spectra of five different positions on the sample. However, since all data was given the almost similar behavior then a one data was selected to the further analysis. By following the same procedure the Raman data for all samples, following settings were used to get the suitable data set.

Sample	Laser Power (mW)	No. of Accumulations	Exposure Time (s)
Apatite	115	3	30
Amazonite	112	3	30
Calcite	75	1	25
Crystal Quartz	100	1	25
Dolomite	75	1	25
Feldspar	115	2	25
Graphite	112	5	30
Mica	112	5	30
Milky Quartz	100	2	30
Rose Quartz	112	1	30
Smokey Quartz	100	1	25

Table 1: The settings that used to get Raman spectra of each sample.

All gathered data was recorded for further analysis.

3.3.3 Calibration of x-axis (Raman Shift (cm^{-1}))

The above described prominent sulphur peaks were used to calibrate the x-axis of the graphs. The obtained peak Raman shifts were plotted against the known peaks values of sulphur. The y axis of the graph was chosen to be the known values and the x axis the graph was chosen to be the obtained values. Then the data was fitted using a linear fit. The relevant best fit line was obtained as $y = 1.0007x + 11.1831$. Using this equation the calibrated Raman shift values were obtained.

3.3.4 Processing Obtained Data for the Analysis

The obtained data sets were consisted with background noise. So, before the analysis process the data sets must go through a noise reduction process. To do that, the data sets were imported to python and using the asymmetric least square (ALS) algorithm the background noise was reduced. Also using the "BaselineRemoval" package in the python the baseline was corrected. The corrected data were fitted using the "Zhangfit" method and applied Savitzky-Golay Filter to increase the smoothness of the data. The obtained data was plotted using the calibrated Raman shifts values using the "Matplotlib" package. Then the data related to prominent Raman peaks were obtained from the plotted graphs.

4 Results and Analysis

4.1 Analysis of Group 1 (Calcite, Dolomite and Apatite)

The Raman spectra of Calcite, Dolomite and Apatite are shown in the fig. between the Raman shift range of 70-1824 cm^{-1} .

Normalized and baseline corrected Raman spectrums are as follows.

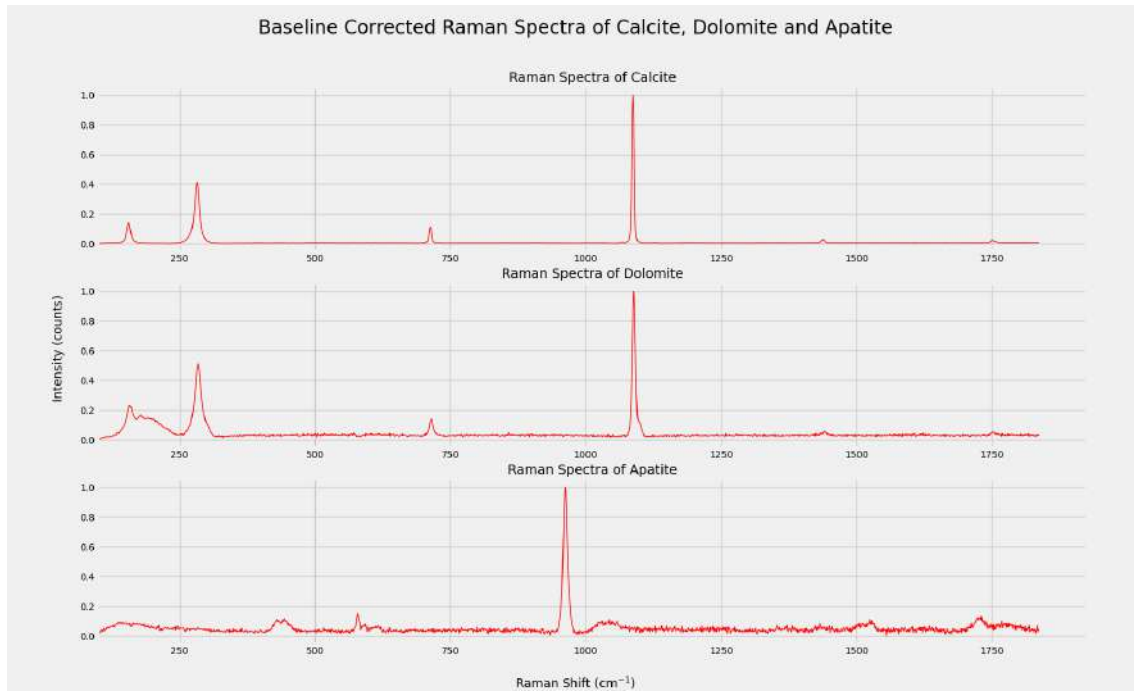


Figure 8: The graphs of baseline corrected data of Calcite, Dolomite and Apatite Samples

In this group, minerals are formed with Calcium. Calcite, Dolomite and Apatite are composed of calcium carbonate (CaCO_3), calcium magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$) and $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH})$, respectively. Calcite and Dolomite are carbonates of Calcium while Apatite has Phosphate instead of Carbonates. They have different Raman peaks due to these variations of bonds. When considering about carbonates, Raman spectra of Calcite and Dolomite have some variations in band position and intensities of CO_3^{2-} group vibrational modes. For the convenience of analyzing, Raman spectra of Calcite and Dolomite can be divided into three regions of Raman shift according to the vibrational mode types [4].

1. 1700–1200 cm^{-1} region attributed to the $(\text{CO}_3)^{2-}$ asymmetric stretching modes
2. 1200–600 cm^{-1} region due to the symmetric stretching of the $(\text{CO}_3)^{2-}$ group
3. 500–100 cm^{-1} region assigned to the external vibrations of the $(\text{CO}_3)^{2-}$ group

4.1.1 1700–1200 cm⁻¹ region

Raman peaks for Calcite can be observed at 1779, 1426 and 1424 cm⁻¹. For Dolomite peaks occur at 1442 and 1761 cm⁻¹. Their intensity values are lower compared to the most prominent peak of the relevant spectra. According to Sun, J et al. [4], peaks occur between 1700-1500 cm⁻¹ region are relevant to water bending modes. And it also points out that peaks between 1400–1200 cm⁻¹ region are due to asymmetric stretching modes of (CO₃)²⁻.

4.1.2 1200–600 cm⁻¹ region

Prominence peak at 1075 cm⁻¹ for Calcite and at 1099 cm⁻¹ for Dolomite can be observed. They are in good agreement with the work from Sun, J et al. [4]. According to that, intense sharp peak at 1088 cm⁻¹ had to appear due to (CO₃)²⁻ symmetric stretching mode.

4.1.3 500–100 cm⁻¹ region

In this region, for Calcite Raman peaks can be observed at 270 cm⁻¹ and 144 cm⁻¹. These peaks are regarding to their external vibrations, which arises from rotatory and translatory oscillations of (CO₃)²⁻ group [5].

For Dolomite Raman peak values can be observed at 302 cm⁻¹ and 178 cm⁻¹. The peak at 302 cm⁻¹ can be attributed to the MgO symmetric stretching vibration and The peak at 178 cm⁻¹ is supposed to be attributed to OMgO bending modes. These values are approximate to the values observed in Sun, J et al. [4].

In Gunasekaran et al. [6] external modes observed in the region 150–190 cm⁻¹ and 285–325 cm⁻¹ are reported as they are due to the relative translations between the cation and anionic groups.

When considering about Apatite, it is composed with phosphate and its Raman spectra are associated with the internal modes of the (PO₄)³⁻ tetrahedral. Vibrational normal modes of these free tetrahedrons are consisting with the group symmetry known as v1, v2, v3 and v4. The v1 frequency is associated with the symmetric stretching of the phosphate and oxygen (P-O) bonds and it is called as A1 symmetry. The v2 frequency associated with the doubly degenerate O-P-O bending modes and known as E symmetry. v3 frequency corresponds to asymmetric P-O stretching which is also known as triply degenerate T2 mode. And v4 frequency is regarding to triply degenerate T2 modes of O-P-O bending character.

Band region related to group symmetry v1, v2, v3 and v4 of (PO₄)³⁻ are 957–962 cm⁻¹, 422–454 cm⁻¹, 1006–1055 cm⁻¹ and 568–617 cm⁻¹ [7]. Observed prominent peaks of the obtained Appetite spectrum are 962 related to v1 symmetry, 430 cm⁻¹, 442 cm⁻¹ and 444 cm⁻¹ related to v2 symmetry, 1025 and 1058 cm⁻¹ related to v3 symmetry and 578 cm⁻¹, 591 cm⁻¹ and 608 cm⁻¹ are related to v4 symmetry of (PO₄)³⁻. Also there are peaks at 1525 cm⁻¹ and 1729 cm⁻¹ they can be assumed due to the other impurities of the Appetite sample. Overall analysis over

there 3 minerals, there most prominent peaks are at 1075 cm^{-1} , 1099 cm^{-1} and 962 cm^{-1} for Calcite, Dolomite and Apatite. These prominent peaks occur due to symmetric stretching mode of $(\text{CO}_3)^{2-}$ of Calcite and Dolomite, and ν_1 group symmetry of $(\text{PO}_4)^{3-}$ in Apatite. These differences in Raman spectra can be used to identify minerals.

4.2 Analysis of Group 2 (Quartz)

In this group, four varieties of quartz are selected for analysis. They are Crystal quartz, Milky quartz, Rose quartz and Smokey quartz. Obtained raw data spectra of them are given below.

Spectra after axis calibrating, baseline correcting and normalizing are given below.

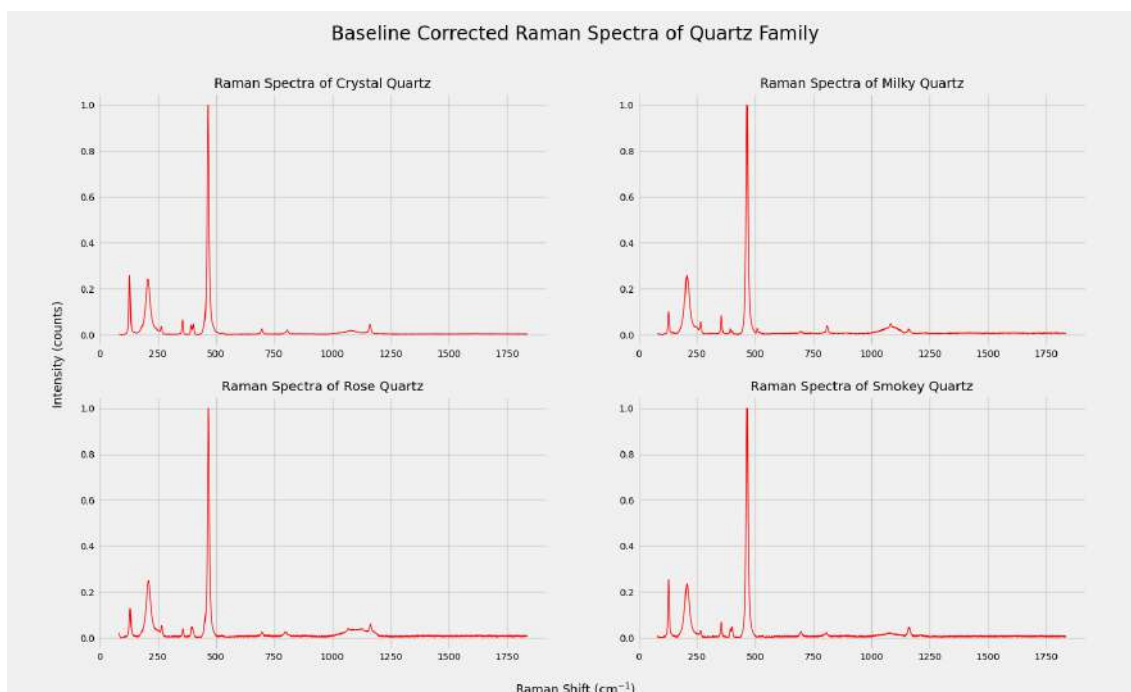


Figure 9: The graphs of Raman spectra of baseline corrected data of Quartz family

As in the above figure, all four spectra have the most prominent peak around 500 cm^{-1} . These peaks occur evidently at 465.87 , 464.69 , 467.04 and 465.87 cm^{-1} for are Crystal quartz, Milky quartz, Rose quartz and Smokey quartz respectively. These peaks occur due to the vibration modes of SiO_2 in quartz. Also, a common peak at 1161.75 cm^{-1} can be observed in the spectrums of Crystal quartz, Milky quartz and Smokey quartz. This peak has a relatively small value compared to the intensity value of the peaks regarding SiO_2 . A similar peak has occurred at 1163.89 cm^{-1} for Rose quartz. Also there can be observed two prominence peaks in the region between $100\text{-}250\text{ cm}^{-1}$ in all four spectrums.

4.3 Analysis of Group 3 (Feldspar)

In this group mineral stones belonging to the Feldspar family is analyzed. A sample of Amazonite and a sample of unknown variety of feldspar are used to obtain Raman spectrums. Raman spectrum of the Feldspar is given below.

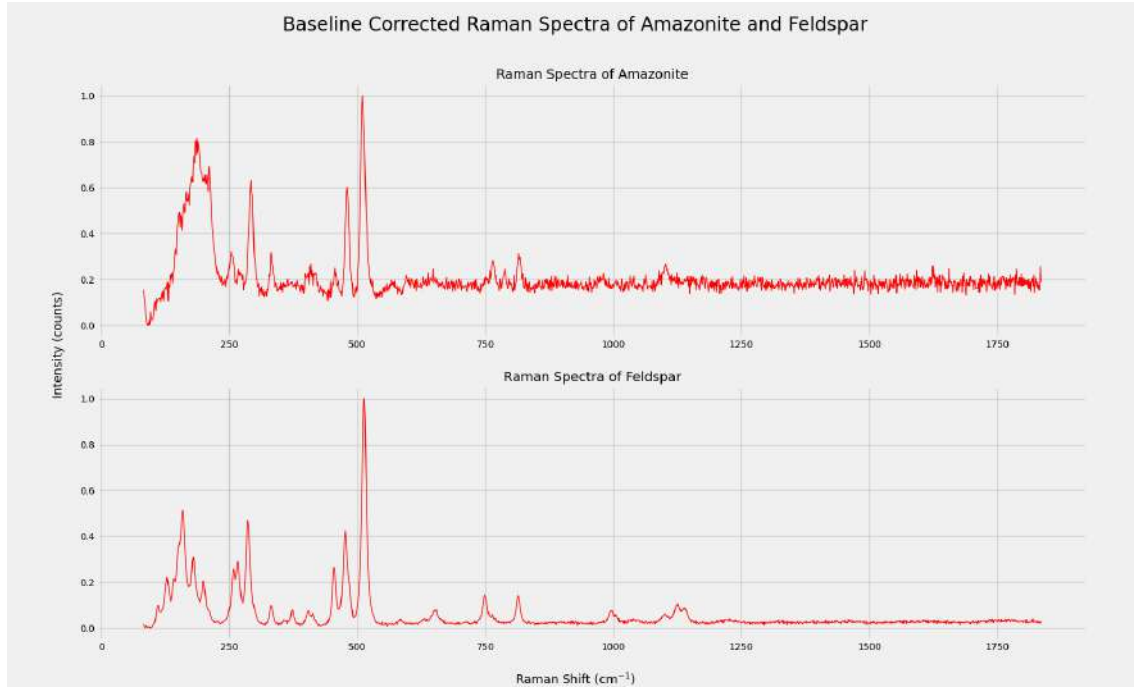


Figure 10: The graphs of baseline corrected data of Amazonite and Feldspar Samples

Shape of the Raman spectra are almost similar for both samples, but number of visible peaks are slightly higher in Amazonite than the Feldspar(unknown) sample. values prominent peaks of Raman spectrum of Amazonite are 186, 212, 253, 268, 270, 291, 331, 408, 457, 479, 510, 596, 764, 787, 815 and 1102 cm^{-1} . Prominent peak values of Raman spectrum of Feldspar(unknown) are 1140, 1133, 996, 813, 749, 654, 513, 476, 454, 412, 404, 372, 331, 285, 266, 257, 199, 179, 158, 128, and 111 cm^{-1} . Most prominent peak occurred at 510 cm^{-1} and 513 cm^{-1} for Amazonite and Feldspar(unknown) sample respectively. These values agree with the Sharma et al [8]. Raman spectra of Feldspar family is recognizable due to the strong peaks appeared between 450 – 515 cm^{-1} region according to Freeman, J. J et al [9]. Feldspar contains TO_4 tetrahedra (T = Si, Al). These occurrence peak positions vary due to the structure of the tetrahedra. Raman peaks between 450-520 cm^{-1} are corresponding to the ring-breathing modes of the four-membered rings of tetrahedra. Peaks below 400 cm^{-1} correspond to the rotation–translation modes of the four-membered rings and cage-shear modes. There are mid-weak peaks occur in 700-900 cm^{-1} region and they are related to the deformation modes of the tetrahedra. And weaker peaks occur between 900 – 1200 cm^{-1} belong to the vibrational stretching modes of the tetrahedra.

4.4 Analysis of Graphite

Raman spectrum of Graphite between the range of 70-1824 cm^{-1} is as follows.

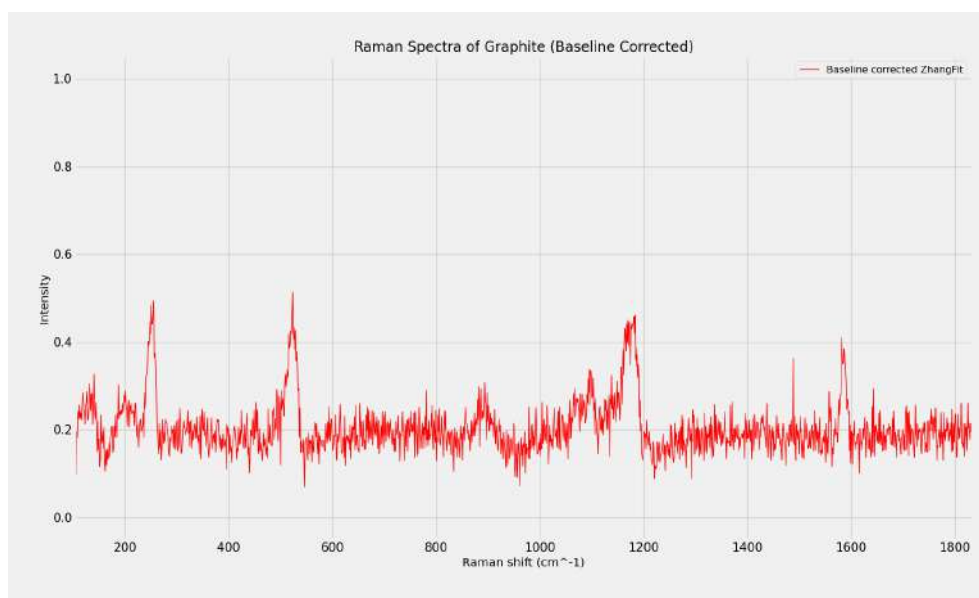


Figure 11: The graphs of baseline corrected data of Graphite

Prominent peak values of graphite are occurring at 200, 254, 585, 893, 1087, 1210, 1485 and 1588 cm^{-1} . The peak occurred at 1088 cm^{-1} is considered to be the G band.

4.5 Analysis of Mica

The Raman spectrum of Mica is as follows.

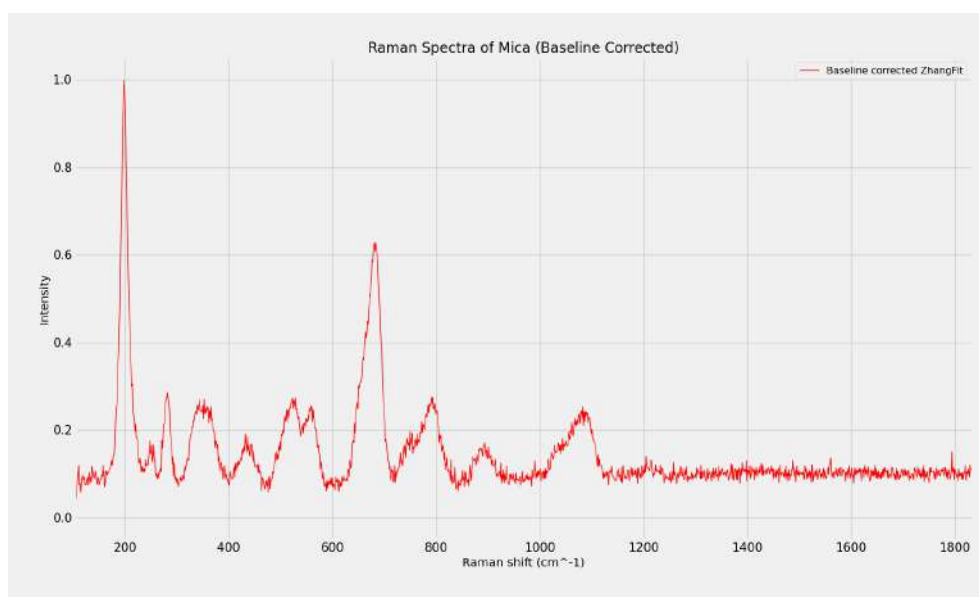


Figure 12: The graphs of baseline corrected data of Mica

There are several Raman peaks that can be observed, and the two most prominent peak values are 187 and 688 cm^{-1} . For the simplicity of the analysis, Raman spectra can be divided into three regions.

4.5.1 Low wavenumber region (70-300 cm^{-1})

Several peaks can be observed in this region and they occurred due to MO₆ octahedron and a strong Raman peak appears at 187 cm^{-1} . According to Tlili et al. [10], a peak around 195 is common in dioctahedral and trioctahedral micas. The sample used to obtain the Raman spectrum is known as Phlogopite, which is a trioctahedral mica.

4.5.2 High wavenumber region (300–1250 cm^{-1})

Strong Raman peak appearance between this region can be observed. The peak at 688 cm^{-1} can be considered as it is due to the Si-O-Si bond in Phlogopite.

5 Discussion and Conclusion

Sri Lanka is enriched with many mineral varieties with high purity. Although Raman Spectroscopy is used to analyse various minerals, there is no data base created on Raman spectroscopy of Sri Lankan minerals. Therefore, in this research project few samples of commonly found minerals around Sri Lanka are analyzed using Raman Spectroscopy. Some of minerals are analyzed group wise, considering their chemical and structural properties and others are analyzed individually.

When considering group 1, which contains Calcite, Dolomite and Apatite; their most prominent peaks were observed at 1075 cm^{-1} , 1099 cm^{-1} and 962 cm^{-1} respectively. Those peaks were assumed to have occurred due to symmetric stretching mode of $(\text{CO}_3)^{2-}$ of Calcite and Dolomite, and ν_1 group symmetry of $(\text{PO}_4)^{3-}$ in Apatite. These differences in Raman spectra can be used to identify minerals. Therefore, Raman spectroscopy is useful to identify the difference between carbonates and phosphates of Calcium [11]. Considering about Carbonates in Calcite and Dolomite peaks between the range of $1700\text{--}1500\text{ cm}^{-1}$ occur due to the water bending modes. It is proposed to have water molecules and intercalated anions in the space of the interlayer [4]. Bands in this region are weakly Raman active hence they have small intensity values. But they are highly infrared active, therefore Fourier transform infrared spectroscopy (FTIR) can be used to analyze them further. Raman peaks between the range of $1400\text{--}1200\text{ cm}^{-1}$ occur due to asymmetric stretching modes of $(\text{CO}_3)^{2-}$. For Calcite there can be observed peaks at 1424 cm^{-1} and 1426 cm^{-1} which is observed to be two peaks around 1425 cm^{-1} . And Dolomite has a peak at 1442 cm^{-1} . These peak values can be used to identify the difference between Calcite and Dolomite. Calcite has a trigonal structure with two molecules per unit cell, and dolomite has a hexagonal structure [4]. In the range of $500\text{--}100\text{ cm}^{-1}$, for Calcite Raman peaks were observed at 270 and 144 cm^{-1} . These peaks are relevant to their rotatory and translatory external vibrations of $(\text{CO}_3)^{2-}$ [2]. For Dolomite Raman peak values can be observed at 302 and 178 cm^{-1} . The peak at 302 cm^{-1} can be attributed to the MgO symmetric stretching vibration and the peak at 302 cm^{-1} is supposed to be attributed to OMgO bending modes. These values are approximate to the values observed in Sun, J et al. [4]. For Dolomite Raman peak values can be observed at 302 and 178 cm^{-1} . The peak at 302 cm^{-1} can be attributed to the MgO symmetric stretching vibration and The peak at 302 cm^{-1} is supposed to be attributed to OMgO bending modes. These values are approximate to the values observed in Sun, J et al. [4]. When considering Apatite, it is composed with phosphate and its Raman spectra are associated with the internal modes of the $(\text{PO}_4)^{3-}$ tetrahedral. Vibrational normal modes of these free tetrahedrons are consisting with the group symmetry known as ν_1 , ν_2 , ν_3 and ν_4 . The ν_1 frequency is associated with the symmetric stretching of the phosphate and oxygen (P-O) bonds and it is called as A_1 symmetry. The ν_2 frequency associated with the doubly degenerate O-P-O bending modes and known as E symmetry. ν_3 frequency corresponds to asymmetric P-O stretching which is also known as e triply degenerate T_2 mode. And ν_4 frequency is regarding to triply

degenerate T2 modes of O-P-O bending character. Band region related to group symmetry ν_1 , ν_2 , ν_3 and ν_4 of $(\text{PO}_4)^{3-}$ are $957\text{--}962\text{ cm}^{-1}$, $422\text{--}454\text{ cm}^{-1}$, $1006\text{--}1055\text{ cm}^{-1}$ and $568\text{--}617\text{ cm}^{-1}$ [4]. Observed prominent peaks of the obtained Appetite spectrum are 962 cm^{-1} related to ν_1 symmetry, 430 , 442 and 444 cm^{-1} related to ν_2 symmetry, 1025 and 1058 cm^{-1} related to ν_3 symmetry and 578 , 591 and 608 cm^{-1} are related to ν_4 symmetry of $(\text{PO}_4)^{3-}$. Also there are peaks at 1525 and 1729 cm^{-1} they can be assumed due to the other substances of the Appetite sample.

The second group consists of four varieties of Quartz, which are named Crystal quartz, Milky quartz, Rose quartz and Smokey quartz. Chemical composition of Quartz is consistent with SiO_2 and their colour will be changed due to the impurities [12]. Crystal quartz contains minimal impurities hence they are colourless or crystal-like. According to chemical analysis, Smokey and Rose quartz have their colour due to the presence of Al and Mn. Milky quartz has their milky colour due to gas and fluid inclusions or the presence of Ca. Although, it is expected to observe a noticeable change in Raman spectra of four varieties, prominence peaks in all spectra are very similar. Most prominent peaks were occurred at 465.87 , 464.69 , 467.04 and 465.87 cm^{-1} for are Crystal quartz, Milky quartz, Rose quartz and Smokey quartz respectively and they are considered to be due to the vibrational modes of SiO_2 . A common peak occurred at 1161.75 cm^{-1} in the spectrums of Crystal quartz, Milky quartz and Smokey quartz. A similar peak was observed at 1163.89 cm^{-1} for Rose quartz. This peak has a relatively small value compared to the intensity value of the peaks regarding SiO_2 . It was not recorded in previously analyzed Raman spectrums of Quartz. Hence this could be due to some impurity specially contains in Sri Lankan quartz. This can be resolved by running some chemical analysis for the samples those are used to obtain Raman spectra. Overall analysis, it was not possible to determine the difference among the Quartz family. In this study solid samples were used to obtain Raman spectrums. X-ray diffraction and FTIR can be used to do further analysis. This method can be continued to obtain Raman spectra of powdered samples. These are Raman spectra of surface of the minerals. More details could be obtained by focusing into inclusions of Quartz, since Milky quartz has its colour due to substances inside inclusions. Also, these samples were not categorized geographically. This study can be extended using samples collected and categorized according to the origin.

The composition of Feldspar has a general formula of AT_4O_8 , where A = Potassium(K), sodium(Na) or Calcium(Ca); and T = Silicon(Si) and Aluminum(Al), with a Si:Al ratio ranging from 3:1 to 1:1. It has the tectosilicate structure which contains TO_4 tetrahedra. There are several Raman peaks occurring due to this tetrahedra structure. Strong Raman peaks can be observed between $450\text{--}520\text{ cm}^{-1}$ including the most prominent peaks at 510 cm^{-1} and 513 cm^{-1} for Amazonite and Feldspar(unknown) sample respectively. According to Freeman, J. J et al [9], Raman spectra of Feldspar can be recognized by the occurrence of strong Raman peaks between this region (between $450\text{--}515\text{ cm}^{-1}$). Peaks below 400 cm^{-1} correspond to the rotation–translation modes of the four-membered rings and cage-shear modes. There are mid-

weak peaks occur in $700\text{--}900\text{ cm}^{-1}$ region and they are related to the deformation modes of the tetrahedra. And weaker peaks occur between $900\text{--}1200\text{ cm}^{-1}$ belong to the vibrational stretching modes of the tetrahedra. As mentioned above, the variation of the ratio of Si to Al is varying for different Feldspar varieties. Therefore several minerals can be seen in Feldspar family, such as Microcline, Orthoclase, Amazonite, and Sanidine etc. One of the sample used to obtain Raman spectra in this research project is Amazonite and the other sample was not declared to be which variety. This study can be extended by using several samples of Feldspar, according to the variety and geographical occurrence. Also X-ray diffraction method and an electron microprobe (EMP) can be used to backup the analysis.

In this study, Raman spectroscopy of Graphite sample is analyzed in the range of $70\text{--}1824\text{ cm}^{-1}$. A special peak at 1088 cm^{-1} is observed and it was declared to be the G band of the Raman spectrum of Graphite. More details about the bonds in Graphite can be obtained by taking the Raman spectrum between different ranges, such as the range between $1700\text{--}2300\text{ cm}^{-1}$ as in Zolyomi et al. [13]. X-ray diffraction method is can also be used for the further analysis.

Finally, the Raman spectrum of Mica was analyzed. The sample that was used to take the Raman spectrum was a Phlogopite or Brown mica, which is rich with Magnesium (Mg). The chemical formula of Phlogopite is $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{F}, \text{OH})_2$. Several peaks were observed in the Raman spectrum of the Mica sample. Two strong peaks appeared at 187 and 688 were declared to be occurred due to the trioctahedral structure of MgO_6 and Si-O-Si bonds of Phlogopite. Several peaks were observed in the Raman spectrum of the Mica sample. Two strong peaks appeared at 187 cm^{-1} and 688 cm^{-1} were declared to be occurred due to the trioctahedral structure of MgO_6 and Si-O-Si bond of Phlogopite according to Tlili et al.[10]. Raman peaks due to other substances can be observed by taking Raman spectra of different regions, such as the region between $3500\text{--}3750\text{ cm}^{-1}$ for the OH stretching modes.

When consider about the overall research project, objective of obtaining Raman spectra of minerals in Sri Lanka was successful. In the first attempt, it was not possible to obtain clear readings from mineral samples. But after cutting and polishing the surface which were intended to focus the laser on, clear spectrums could be obtained. In the analysis, obtained peaks were agreed with the experiments conducted previously. But there were some unidentified peak values too. They require further chemical, X-ray diffraction or FTIR analysis to identify them accurately. This Raman setup was designed to obtain surface details. It was not capable of focusing on an exact point more precisely. This can be solved by combining the Raman spectrometer with a microscope. Specially, mineral sand can be analyzed by using a Raman spectrometer combined with an Scanning Electron Microscope (SEM). Also these minerals are stones with non-homogeneous composition. To overcome this matter Raman spectra of few points were obtained for analysis. This method is not capable of analyzing inclusions of minerals, which could contain important details about the relevant mineral. Inclusions can be analyzed by cutting a surface near to an inclusion. And powder of minerals also can be used

for this analysis. Finally, it can be concluded that the Raman spectroscopy is a non-destructive and an effective analysis method for analyze minerals.

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6 Appendix

6.1 Python code to generate subplots

```
1 import numpy as np
2 import matplotlib.pyplot as plt
3 import numpy.polynomial.polynomial as poly
4 from BaselineRemoval import BaselineRemoval
5 from scipy import sparse
6 from scipy.sparse.linalg import spsolve
7 from scipy.signal import savgol_filter
8 from scipy.signal import find_peaks
9 import datetime as dt
10 import os
11
12 plt.style.use('fivethirtyeight')
13 plt.rcParams["mathtext.fontset"]
14 plt.rcParams['font.size'] = '12'
15 plt.rcParams['xtick.labelsize'] = '10'
16 plt.rcParams['ytick.labelsize'] = '10'
17 plt.rcParams['legend.title_fontsize'] = '10'
18
19
20 laser=532;
21 win_size = 6
22 Poly = 5
23
24 file_path='Data Files/' #Give the path to the folder
25 Main_name= 'Main Name' # Main name to name the figures
26
27 #Replace Files Here
28
29 file_1='Amosonite_30s_112mW_3acc_1200gr_532nm_position_03_mms0_05.asc'
30 file_2='Graphite_30s_112mW_5acc_1200gr_532nm_position_01_mms0_05.asc'
31 file_3='Mica_30s_112mW_5acc_1200gr_532nm_position_01_mms0_05.asc'
32 file_4='Smokey_Qartz_25s_100mW_single_1200gr_532nm_position_02.asc'
33
34 file_names=[file_1,file_2, file_3, file_4]
35
36
37 data_matrix = np.zeros((1600, 3))
38 for i,filename in enumerate(file_names):
39     def load_data(filename):
40         data=np.loadtxt(open(filename,'rt').readlines()[::-32])
41         w=data[:,0]
42         s=data[:,1]
43         s = np.array(s)
```

```

44     w = np.array(w)
45     return w,s
46
47 def baseline_als(y, lam,lam1, p, niter=10):
48     L = len(y)
49     D = sparse.diags([1,-2,1],[0,-1,-2], shape=(L,L-2))
50     D1 = sparse.diags([1,-1],[0,-1], shape=(L,L-1))
51     w = np.ones(L)
52     for i in range(niter):
53         W = sparse.spdiags(w, 0, L, L)
54         Z = W.dot(W.transpose()+lam1 * D1.dot(D1.transpose())) + lam * D.
dot(D.transpose())
55         b=(W.dot(W.transpose()+lam1 * D1.dot(D1.transpose()))).dot(y)
56         z = spsolve(Z, b)
57         w = p * (y > z) + (1-p) * (y < z)
58     return z
59
60 def apply_baseline():
61     w, s = load_data(file_path+filename)
62     baseline = baseline_als(s,100,0.0000000005,0.000098)
63     #0.000000005,0.000098 # window size,traces the dents, shape
64     corrected = s- baseline
65     return baseline, corrected
66
67 def Zhang_fit():
68     w, s = load_data(file_path+filename)
69     baseobj = BaselineRemoval(s)
70     zhang_out = baseobj.ZhangFit()
71     return zhang_out
72
73 Zhang_fit()
74
75 def calibrating_wavelengths(x):
76     cal_wav = 1.0006821140902764*x+11.183084552457835
77     return cal_wav
78
79 def plot_base(win_size, poly):
80     w, s = load_data(file_path+filename)
81     baseline, corrected = apply_baseline()
82     Zhangfit_output = Zhang_fit()
83
84     corrected=savgol_filter(corrected, win_size, Poly)
85
86     def normalize(intensity):
87         intensity = intensity - np.min(intensity)
88         intensity = np.interp(intensity, (0, np.max(intensity)), (0, 1))

```

```

89         return intensity
90
91         normalized_intensity = normalize(Zhangfit_output)
92
93         data_matrix[:, i] = normalized_intensity
94         print(len(normalized_intensity))
95         plot_base(win_size, poly)
96
97 w, s = load_data(file_path+filename)
98
99 print(len(w))
100 fig5, axs = plt.subplots(nrows=3, ncols=1, figsize=(10, 8))
101 axs[0].plot(calibrating_wavelengths(w), data_matrix[:,0].reshape(-1,1),
102             linestyle='-', linewidth=1, color='red')
103 axs[0].set_title('Raman Spectra of Amazonite',fontsize="14",math_fontfamily
104                 ='cm')
105 axs[0].set_xlim(left = 100)
106 axs[1].plot(calibrating_wavelengths(w), data_matrix[:,1].reshape(-1,1),
107             linestyle='-', linewidth=1, color='red')
108 axs[1].set_title('Raman Spectra of Graphite',fontsize="14",math_fontfamily
109                 ='cm')
110 axs[1].set_xlim(left = 100)
111 axs[2].plot(calibrating_wavelengths(w), data_matrix[:,2].reshape(-1,1),
112             linestyle='-', linewidth=1, color='red')
113 axs[2].set_title('Raman Spectra of Mica',fontsize="14",math_fontfamily='cm
114                 ')
115 axs[2].set_xlim(left = 100)
116
117 fig5.suptitle("Baseline Corrected Raman Spectra of Calcite, Dolomite and
118               Apatite", fontsize = "20")
119 fig5.text(0.5, 0.005, 'Raman Shift (cm$^{-1}$)',fontsize="13", ha="center")
120 fig5.text(0.04, 0.5, 'Intensity (counts)', va='center', rotation='vertical
121             ',fontsize="13")
122 plt.show()

```

6.2 Python code to generate single plots

```

1
2 import numpy as np
3 import matplotlib.pyplot as plt
4 import numpy.polynomial.polynomial as poly
5 from BaselineRemoval import BaselineRemoval
6 from scipy import sparse
7 from scipy.sparse.linalg import spsolve
8 from scipy.signal import savgol_filter
9 from scipy.signal import find_peaks

```

```

10 import datetime as dt
11 import os
12
13 plt.style.use('fivethirtyeight')
14 plt.rcParams['font.size'] = '12'
15 plt.rcParams['xtick.labelsize'] = '15'
16 plt.rcParams['ytick.labelsize'] = '15'
17 plt.rcParams['legend.title_fontsize'] = '15'
18
19
20 laser=532;
21
22 file_path='/Users/saan/Desktop/APL-GROUP C/Project/Data Files/' #Give the
    path to the folder
23 Main_name= 'Main Name' # Main name to name the figures
24 file_name='Graphite_30s_112mW_5acc_1200gr_532nm_position_02_mms0_05.asc' #
    Usual file name
25 figure_folder='/Users/saan/Desktop/Test' #Image folder name to be created
26 os.makedirs(figure_folder, exist_ok = True)
27
28 #Sav_gol parameters
29 win_size = 6
30 Poly = 5
31
32 #calibrating x-axis
33 prominent_sulfar_peaks = []
34
35 def load_data(file_name):
36     data=np.loadtxt(open(file_name,'rt').readlines()[:-33])
37     #data=np.loadtxt(file_name,delimiter='\t')
38     w=data[:,0]
39     s=data[:,1]
40     s = np.array(s)
41     w = np.array(w)
42     return w,s
43
44 # Asymmetric Least Squares Method
45 def baseline_als(y, lam,lam1, p, niter=10):
46     L = len(y)
47     D = sparse.diags([1,-2,1],[0,-1,-2], shape=(L,L-2))
48     D1 = sparse.diags([1,-1],[0,-1], shape=(L,L-1))
49     w = np.ones(L)
50     for i in range(niter):
51         W = sparse.spdiags(w, 0, L, L)
52         Z = W.dot(W.transpose()+lam1 * D1.dot(D1.transpose()) + lam * D.dot(D.
            transpose()))
53         b=(W.dot(W.transpose()+lam1 * D1.dot(D1.transpose()))).dot(y)

```

```

54     z = spsolve(Z, b)
55     w = p * (y > z) + (1-p) * (y < z)
56     return z
57
58 # Plotting the Raw data
59 def plot_raw():
60     w, s = load_data(file_path+file_name)
61     print('w = ',w)
62     fig, ax = plt.subplots(figsize=(12,6))
63     ax.plot(w,s, linestyle='-', linewidth=1, color='blue',label='Raw')
64     plt.title('file_name[:-4]' + '_Raw')
65     plt.xlabel('Raman shift (cm-1)')
66     plt.ylabel('Intensity')
67     ax.legend()
68     plt.tight_layout()
69     plt.savefig('figure_folder+'/'+Main_name+ '_Raw' + "_" + dt.datetime.now
70     ().strftime("%Y%m%d%H%M%S")+'.png')
71     plt.show()
72
73 # Apply baseline and correction
74 def apply_baseline():
75     w, s = load_data(file_path+file_name)
76     baseline = baseline_als(s,100,0.0000000005,0.000098)
77     #0.0000000005,0.000098 # window size, traces the dents, shape
78     corrected = s- baseline
79     return baseline, corrected
80
81 #Baseline removal from packag
82 def Zhang_fit():
83     w, s = load_data(file_path+file_name)
84     baseobj = BaselineRemoval(s)
85     zhang_out = baseobj.ZhangFit()
86     return zhang_out
87
88 Zhang_fit()
89
90 # Plot baseline and baseline corrected
91 def calibrating_wavelengths(x):
92     w, s = load_data(file_path+file_name)
93     cal_wav = 1.0006821140902764*x+11.183084552457835
94     return cal_wav
95
96 def plot_base(win_size, poly):
97     w, s = load_data(file_path+file_name)
98     baseline, corrected = apply_baseline()
99     Zhangfit_output = Zhang_fit()

```

```

99
100 def normalize(intensity):
101     intensity = intensity - np.min(intensity)
102     intensity = np.interp(intensity, (0, np.max(intensity)), (0, 1))
103     return intensity
104
105 normalized_intensity = normalize(Zhangfit_output)
106
107 #Plotting Raw and Baseline plot
108 fig, ax = plt.subplots(figsize=(12,6))
109 ax.plot(w,s, linestyle='-', linewidth=1, color='blue',label='Raw Data')
110 #ax.plot(w,baseline,linestyle='-', linewidth=1, color='red',label='
Baseline')
111 plt.xlim(104,1833)
112 plt.xlabel('Raman shift (cm-1)')
113 plt.ylabel('Intensity')
114 ax.legend()
115 plt.title('Raman Spectra of Apatite (Raw Data)')
116 plt.tight_layout()
117 #plt.savefig(figure_folder+'/'+Main_name+'_Baseline'+"_"+dt.datetime.
now().strftime("%Y%m%d%H%M%S")+'.png')
118 plt.show()
119
120 '''
121 #Plotting Baseline corrected plot
122 fig1, ax1 = plt.subplots(figsize=(12,6))
123 ax1.plot(w,corrected,linestyle='-', linewidth=1, color='red',label='
Baseline corrected')
124 plt.xlabel('Raman shift (cm-1)')
125 plt.ylabel('Intensity')
126 ax1.legend()
127 plt.title(file_name[:-4] + '_Baseline corrected')
128 plt.savefig(figure_folder+'/'+Main_name+'_Baseline corrected'+"_"+dt.
datetime.now().strftime("%Y%m%d%H%M%S")+'.png')
129 #plt.show()
130 '''
131 #Apply Savitzky-Golay Filter and finding peaks
132 corrected=savgol_filter(corrected, win_size, Poly)
133 peaks = find_peaks(Zhangfit_output,height=270)[0]
134 list_peaks = []
135 for i in range (0,len(peaks)):
136     list_peaks.append(calibrating_wavelengths(w)[peaks[i]])
137 list_peaks.sort(reverse=True)
138 print(list_peaks)
139
140 '''
141 #Savitzky-Golay applied plot

```

```

142     fig3, ax3 = plt.subplots(figsize=(12,6))
143     ax3.plot(w,corrected,linestyle='-', linewidth=1, color='red',label='
Baseline corrected sav_gol')
144     plt.xlabel('Raman shift (cm-1)')
145     plt.ylabel('Intensity')
146     ax3.legend()
147     plt.title(file_name[:-4] + '_Baseline corrected sav_gol')
148     plt.tight_layout()
149     plt.savefig(figure_folder+'/' +Main_name+'_Baseline corrected sav_gol'+
_+"_"+dt.datetime.now().strftime("%Y%m%d%H%M%S")+'.png')
150     #plt.show()
151     '''
152
153
154     #ZhangFit applied plot
155     fig4, ax4 = plt.subplots(figsize=(12,6))
156     ax4.plot(calibrating_wavelengths(w),normalized_intensity,linestyle='-',
linewidth=1, color='red',label='Baseline corrected ZhangFit')
157     plt.xlim(104,1833)
158     plt.xlabel('Raman shift (cm-1)')
159     plt.ylabel('Intensity')
160     ax4.legend()
161     plt.title('Raman Spectra of Graphite (Baseline Corrected)')
162     plt.tight_layout()
163     #plt.savefig(figure_folder+'/' +Main_name+'_Baseline corrected ZhangFit
'+_+"_"+dt.datetime.now().strftime("%Y%m%d%H%M%S")+'.png')
164     plt.show()
165
166
167
168 plot_base(win_size, poly)

```