INDIAN JOURNAL OF SCIENCE AND TECHNOLOGY

ORIGINAL ARTICLE

Spectroscopic Studies (FTIR, XRD, EDX with SEM) and Elemental Analysis (XPS) on Sedimentary Rocks of Pachamalai Hills, Tamil Nadu, India

K. Surendar[1,2]*, P. Rajkumar[3], V. Balachandran[1], K. Sasikumar[2]

1 Department of Physics, Arignar Anna Government Arts College, (Affiliated to Bharathidasan University, Tiruchirappalli-620024, Tamil Nadu, India), Musiri, Tiruchirappalli-621211, Tamil Nadu, India
2 Department of Physics, Urumu Dhanalakshmi College, (Affiliated to Bharathidasan University, Tiruchirappalli-620024, Tamil Nadu, India), Tiruchirappalli-620019, Tamil Nadu, India
3 Department of Physics, Thiruvalluvar Government Arts College, (Affiliated to Periyar University, Salem-636011, Tamil Nadu, India), Rasipuram, Namakkal - 637401, Tamil Nadu, India

OPEN ACCESS

Received: 17/02/2025
Accepted: 29/04/2025
Published: 11/05/2025

Citation: Surendar K, Rajkumar P, Balachandran V, Sasikumar K (2025) Spectroscopic Studies (FTIR, XRD, EDX with SEM) and Elemental Analysis (XPS) on Sedimentary Rocks of Pachamalai Hills, Tamil Nadu, India. Indian Journal of Science and Technology 18(17): 1321-1334. https://doi.org/10.17485/IJST/v18i17.311

* **Corresponding author**.

surenkphy@gmail.com

Funding: None

Competing Interests: None

Published By Indian Society for Education and Environment (iSee)

ISSN
Print: 0974-6846
Electronic: 0974-5645

Abstract

Objective: To investigate the presence of minerals and elements in sedimentary rocks of Pachamalai hills which is located in Tamil Nadu state, South India by suitable spectroscopic techniques such as FTIR, XRD, EDX with SEM and XPS. **Methods:** The FTIR technique has been carried out to identify the minerals and XRD analysis is made for confirmation of identified minerals. EDX with SEM used to determine the surface structure, internal morphology and superficial elemental profile. XPS technique could be used in line profiling of the elemental composition across the surface or in-depth profiling when paired with ion etching. **Findings:** The minerals such as Quartz, Calcite, Cristobalite, Gibbsite, Goethite, Halloysite, Hectorite, Illite, Kaolinite, Lepidocrocite, Microline Feldspar, Montmorillonite, Nacrite, Organic Compound, Palygorskite, Sepiolite, and Siderite are identified. The minerals were identified from the IR absorption band of the location of different peaks. This study demonstrates the Nature of Crystallinity, which was calculated by Crystalline Index of the Rock cementation in elevation wise from Top to Bottom are discussed. The EDX with SEM and XPS gives detailed availability of elements in the middle site of the hill. **Novelty:** The crystalline nature of the hills revealed in non-uniform pattern, this property randomly varies (0.63 – 1.39) in almost all the locations. Their elemental composition is measured in EDX and XPS as well. From EDX results the atomic weight percentage of elements are C – 23.43%, O – 52.24%, Na – 0.86%, Mg – 0.74%, Al – 7.29%, Si – 11.4%, S – 0.07%, K – 0.27%, Ca -1.4%, Ti – 0.11%, Fe – 2.12% and Cu – 0.08%. XPS results revealed O 1s - 58.2%, C 1s - 24.1%, Si 2p - 13.0%, Fe 2p3 – 4.8%, Mg 2s, Ca 2p, K 2p and S 2p are less than 1%.

Keywords: FTIR; XRD; EDX with SEM; XPS; Nature of crystallinity

1 Introduction

Hills are the most valuable natural treasure of minerals, incorporating a large group of metals necessary for an increasing number of industrial and technological applications which develops the national economy. The enormous expansion of industry and infrastructure has increased the consumption and utilization of minerals especially from sand and rocks. The physical, chemical and microstructure studies yield the utility in construction applications [1], [2], [3]. Even small amounts of clay minerals could reveal the information about the properties of petroleum reservoirs and most well logging tools as well. IR Spectra qualitatively related to the variations of constituents of minerals and investing the crystalline structure, type of bonding and some chemical information about the clay minerals. The clay minerals contain the hydroxyl group, tetrahedral and octahedral sheets and interlayer cation gives valuable information about the bending vibration bands of Si-O, Al-O, O-H [2].

The properties of rocks are of great importance in engineering science such as petroleum, mining and civil engineering and also in physic-chemical, geomechanical properties having various applications in different clay minerals and porous rocks [4]. The absorbed IR radiation by individual clay minerals are determined by strength, length and force constants of chemical bonds in their structure of clay minerals and their crystalline order, shape and size too. In nature clay minerals are often accompanied by Quartz, K-Feldspar, plagioclase, carbonates, iron oxide and/or sulphide or sulphates [2].

Many of the resources are not uniformly distributed, in horizontal space and vertical depth. Their qualitative occurrence of minerals and elements are highly varied. Nowadays the useful tools FTIR, XRD, EDX and XPS play a vital role for qualitative analysis of sedimentary rock samples in order to study the identification of minerals, band nature, chemical composition and morphological studies of minerals [3]. Phosphate rocks contribute to providing necessary nutrients for the growth of cultivated plants, they are used in various fields such as production of chemicals, disinfectants, biomaterials applications and different food products [5].

Illite, Kaolinite and Bentonite are the most abundant clays in sandstone, the illite is the most frequent clay mineral in marine shales with a 2:1 structure of a high cation exchange capacity that allow it to absorb and retain much water [6]. Investigation of rock samples for authentication should focus on long term interaction between objects and environments, resulting in unique compositional and micro structural characteristics absent in modern limits. It gives archaeological information too [7]. The element composition obtained by EDX analysis gives the provenance of artifacts, the representations grouped based on their chemical profile. The finding of oxides ratio helps to confirm the results of chemo metric analysis [8]. The collected data via FTIR, XRD, EDX with SEM and XPS greatly enhance the information acquired by the preliminary studies and allow a complete characterization of binder and aggregate fractions. It is necessary to understand chemical and morphological composition, texture, microstructure and grain size distribution to generate a final product for effective conservation [9], [10]. The chemical composition and mineralogical assemblage of the samples indicated to use of calcareous raw materials [11].

The rocks clay minerals have been the subject of several studies utilized to gain the information to characterize the depositional environment and evaluate their mineralogical potential. The interest of clay and metallic mineral studies has multiple applications as water treatment materials, paint components, barriers against pollutants, adsorbent substances, catalysts and as drilling fluids etc. Knowledge of mineralogical composition of these source rocks will determine if they present risk of swelling, a phenomenon that causes jamming of drilling rig and drilling bit [12].

As southern India is a part of tropical climatic zone where the lateralization process is predominant, the present study can reveal new information on the dynamics involved in the formation and development of soil profiles. The rock iron oxide minerals like Goethite and Hematite, and clay mineral Kaolinite and Gibbsite are giving the much needed information about the magnetic characterization [13]. Understanding the composition of sedimentary rocks (sandstone, shales, carbonates and evaporates) is of great importance because the pore volume and connectivity of prenetworks in the sedimentary rocks provide a location for CO_2 storage and conduits for CO_2 flows. Sedimentary rocks formed either as detrital or clastic sediments that are transported and deposited by different environments [14]. Iron oxides are the main components of the sedimentary iron ore deposits which comprise 80% of the world's iron ore productions. The main group of the sedimentary iron ores, termed iron stones, are defined as non-cherty, sandy, fine-grained, or siliciclastic-carbonate sedimentary rocks with less than 15% weight percentage of iron [15].

The Fourier transform infrared (FTIR) analysis, spectral scanning about 4000-500 cm^{-1} wavenumber to evaluate mass rock powered samples and its peak analysed the essential minerals. The mineralogical identification of the rock materials were further analyzed by X-ray diffractometer (XRD) is an analytical technique for identifying minerals and other crystalline phases in sedimentary rocks. The diffractrogram follows Bragg's law for calculating the resulting angle, which is crystalline phase dependent [16]. This technique is adopting panalytical X'pert PRO MPD (PW3040/60) diffractometer with X'celertor detector having CuKα radiation and an X-ray ceramic tube. The scanning range was 10° to 80°, 2θ, 30mA and 40 kV, 60 s time/step and 0.02° advanced step size, anti-scattering of 1/4° and divergent slit of 1/8°. The experimental spectral patterns were matched with patterns received from the international centre for Diffraction Data (ICDD) or Joint Committee on Powder

Diffraction Standard (JCPDS) database and match. EDX with SEM (Electron Dispersive X-ray Spectrometer with Scanning Electron Microscope) were set up by scattering dry powder on both sided conductive sticky tape. Tests were covered with carbon by curve release technique for EDX with SEM and the dried rock powered samples. The SEM pictures were examined using the programming image J. The surfaces of the particles were scanned and the elemental composition with arrangement was determined by energy-dispersive X-ray spectrometry attached to SEM. The outcome was detected and recorded with the Genersis 60E programming[17]. X-ray photoelectron spectroscopy (XPS) allows the direct quantification of elements and its functionalities. The shift on baseline around C1s signal and the method with a high signal-to-noise ratio is required to evaluate the quantities[18].

The Pachamalai hills possess good biodiversity in plants and animals as well. This paper aimed to investigate the mineral and element content occurrence and their nature of crystallinity of the rock samples.

2 Methodology

Pachamalai hills located in south india with GPS coordinates are 11.3258°N, 78.6308°E, Tamil Nadu State, it is situated at a distance of 73 km from Tiruchirappalli district, 112 km from Salem district and 40 km from Perambalur district and it is spread over in these three districts and the location map shown in Figure 1. But most of the places are located in Tiruchirappalli district. These hills extend over an area about 190 square km, and they form discontinuous lines of heights; elevation ranges from 540 m to 1400 m. The people who lived in the pachahamalai hills were named as Pachamalayalies. This Eastern Ghats low mountain regions have good biodiversity in plants and spices. Sweata River and Kallar River are two main rivers as water source for these hills and it includes Koraiyar falls, Mangalam Falls and Mayil uthu water falls for the water sources for drinking and agriculture as well. This rock is assembled with minerals such as Quartz, Hornblende, Biotite, K-Feldspar and Plagioclase.

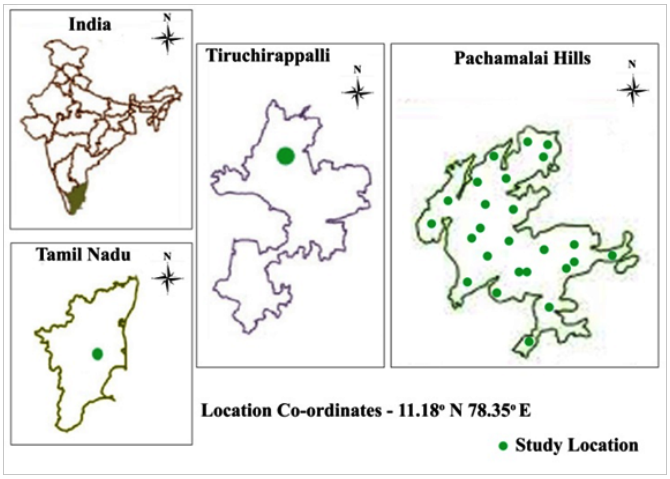

Fig 1. Location of Pachamalai Hills

2.1 Sample Collection and Preparation

Twenty five different locations were selected at various altitudes randomly with at least 500 m away from each location of the mountain and the rock samples are collected around 1 Kg from each location and stored in self lock thick polythene bags. The rock samples are numbered as P-1 to P-25.

All the samples were brushed, cleaned with distilled water and weathered on the surface for an hour in order to remove moisture. The samples were crushed into small stones. These stones were ground into fine powder, by taking 30-50 mg and grinding in an agate mortar for 15-20 minutes till to get expected size.

2.2 FTIR

Fourier Transform Infra-Red Spectroscopy is an essential tool to identify the minerals with absorption wave number. The Perkin Elmer RXI FTIR Spectrometer is used to analyse the samples in mid region infrared wavelengths of 4000 – 400 cm^{-1} at room temperature. The selected powdered rock samples were crushed and ground KBr was mixed with a ratio of 1:40. In one minute

it could scan the spectra 100 times with resolution of 0.001 cm^{-1} with accuracy of 4 cm^{-1}. The standard polystyrene film was used every time the calibration of instruments for their accuracy with the spectrum. OPUS 6.5 software was used to record the peaks.

2.3 XRD

The X Ray diffraction patterns were recorded in room temperature for same locations of twenty five powdered rock samples using Seifert (JSO-DEBYEFLEX 2002). Each 0.5 mg sample was homogeneously dispersed in a cover glass which served as a sample holder in the X Ray diffractometer. This instrument has a curved graphite crystal diffracted monochromator, CuKα radiation as a source with λ = 1.5406 Å, the patterns were recorded in 2θ range from 20° to 80° and Nal (Tl) scintillation detector.

2.4 EDX with SEM

Energy Dispersive X Ray Spectrometer (EDX), the emission of X rays determined the elemental composition for elemental identification during Scanning Electron Microscopic (SEM) observations. The morphological investigations were done on JEOL, JSM 6390 scanning electron microscope with 20 V accelerating voltage and a beam current of 1-3 nA. The SEM images were revealed by either secondary electrons or back scattered electrons.

2.5 XPS

X Ray Photoelectron Spectroscopy (XPS) is a powerful tool to identify the elements present in the samples and also what other elements were bonded to. This technique could be used in line profiling of the elemental composition across the surface or in-depth profiling when paired with ion etching. It provides the information about the oxidation and structural state parameters of the iron oxides and to determine the surface chemistry of the investigated ironstones to a depth less than 10 nm[15].

3 Results and Discussion

3.1 FTIR - Determination and Characterization of Minerals

Fourier Transform Infrared (FTIR) spectroscopy technique results of Figure 2 show the absorption of the infrared spectrum with band assignment and respective minerals with respect to their suitable frequency at site number 03. The comparison of 25 samples of FTIR spectra which are collected from all locations has shown in Figure 3. The tentative band assignment and occurrences of the minerals consolidated with their wave numbers are tabulated in Table 1.

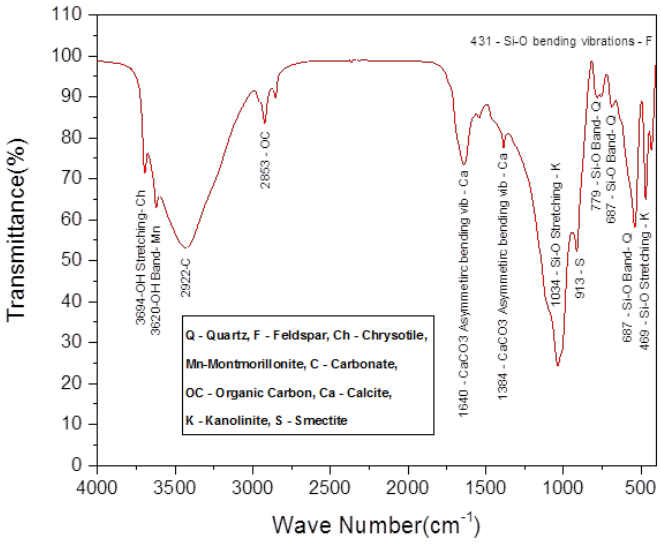

Fig 2. FTIR Spectrum at Site location 03

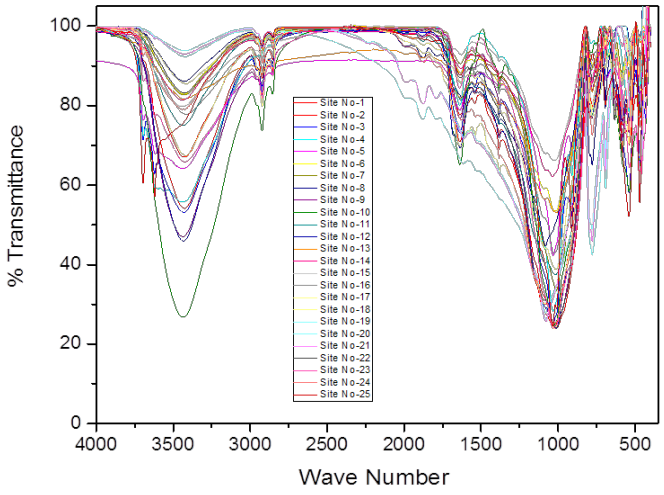

Fig 3. Comparison of FTIR Spectra of Pachamalai Hills at Site locations (1-25)

Table 1. FTIR absorption identification of Minerals with Band assignment of Pachamalai Hills

S. No	Mineral Name	Chemical Formula	Wave No	Band Assignment	Site Number
1	Quartz	SiO_2	1882 - 1870	Si-O Band	11-15,19-21,24
			1616 - 1613	Si-O Band	19,20,21
			1082	Si–O -band	19
			795 & 794	Si–O stretching	21,25
			783 & 782	Si–O symmetrical stretching	7,10
			781-779	Si–O stretching	2,3,20
			778	Si-O broad	1,8-18,21
			777	Si–O symmetrical stretching	6,11-19,22,24
			695 - 678	Si-O Symmetric bending vibration	1 to 25
			677	Si-O Symmetric bending vibration	9
			514	Si-O-Si asymmetrical bending	21
			489	Si-O Stretching Mode	6
			468 - 464	Si–O–Si bending	1-9,23,16-22
			461	Si-O-Si asymmetrical bending	12
			458	Si-O asymmetrical bending vibrations	18
			434, 433	Si-O bending vibrational bands	9,16,17,24
2	Kaolinite	$Al_4Si_4O_{10}(OH_8)$	3695	Plane declined vibration of H2O	25
			3693	OH elongation mode	4,5
			3418	symmetric elongation vibration	16,17,18
			1635		7
			1036 - 1028	Si–O stretching (clay mineral)	1-5,10,12-16,23,24
			1020 & 1014	Si-O stretching	6,12
			538		1,2,14

Continued on next page

Table 1 continued

			471 - 469		3,1024,25
3	Calcite	$CaCO_3$	1640 - 1638		3-5,10,23
			1384 - 1383	CaCO3 asymmetrical bending vibration	1-5,8-12,16,17,22-24
			1790	Al–O coordination vibrations	21
4	Feldspar	$AlSiO_3O_8$	639	Al–O coordination vibrations	7
			586 - 582	O-Si(Al)-O bending vibrations	6-18,22-24
			535	Al-O-coordination vibrations	7
			465		Nov-15
			431	Si-O bending vibrations	3
			2852 & 2051		8,16,19,21-24
5	Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2,(H_2O)$	1637 - 1627	H–O–H stretching	1-6,9,11-18,22-25
			755		25
			3620	OH band	3,25
			3441 - 3431	H–O–H stretching of water molecules	3,12,15,24
6	Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2\ nH_2O$	3423	H–O–H stretching of water molecules	1
			1025	H–O–H stretching of water molecules	17
			911 & 910	MVI-OH low-precision deflection vibration	4,5,25
			540 - 536	C-X [X=Cl, Br, I]	3-13,15-18,22-25
7	Hematite	$\alpha - Fe_2O_3$	524 - 520	Si–O–Al (or) Fe2O3	8,20
	Organic		2924		5,14,15,25
8	Carbon	C	2855 - 2853	Organic matter	1-3,6,9-12,20,25,
			2922 - 2920	Organic matter	1-3,8,13,16-24
9	Carbonate	CO_3^{2-}	1797		20
10	Diopside	$CaMgSi_2O_6$	634 - 630	S-O-Si bending	1,2,6-9,11-13,16,17,22-24
11	Hectorite	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2$	1013 - 1011	Si-O stretching band	1,9,13,18
12	Chrysotile	$Mg_3Si_2O_5(OH)_4$	3694	OH stretching region	3
13	Smectites	$M_{0.33}{}^{+}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$ M^+ represents exchangeable cations like Ca^{2+} and Mg^{2+}	3430	H-O-H stretching vibration	6
14	Magnesium -rich chlorite	Cl_2MgO_4	1630		14
15	Water molecules absorbed or present	H_2O	1623	H-O elongation	8
16	Wollastonite	$CaSiO_3$	1080 -1079	Si-O-Si absorption	8,20,21
17	Anhydrite	$CaSO_4$	1015		11
18	Saponite	$(Na,Ca)_{0.25}Mg_3(Si,Al)_4O_{10}(OH)_2.4H_2O$	1010	Si-O stretching band	22,25
19	Smectite	$M_{0.33}{}^{+}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$ M^+ represents exchangeable cations like Ca^{2+} and Mg^{2+}	913		3
20	Anorthite	$CaAl_2Si_2O_8$	753 & 752	Si-Al(Si) stretching	4,5
21	Goethite	α-Fe(OH)O	637 - 635		18,14,15

Continued on next page

Table 1 continued

22	Albite	$NaAlSi_3O_8$	581 & 579	O-Si-O bending	1,14
23	Magnetite	Fe_3O_4	575		2
24	Goethite	α-Fe(OH)O	459		21
25	Sepiolite	$(Na,Ca)_{0.25}Mg_3(Si,Al)_4O_{10}(OH)_2.4H_2O$	432		22,25

3.1.1. ***Quartz (SiO_2)***

Quartz is an important mineral in sand and rock as well, in Pachamalai Hills almost all the locations of this mineral is revealed. In the wavelength region 1882-1870 cm^{-1}, 1616-1613 cm^{-1}, 1082 cm^{-1} and 778 cm^{-1} shows the availability of Quartz [1]-[8],[?] in various site numbers like (11-15,19-21,24). Si–O symmetric stretching vibration region proves the presence of Quartz mineral in the site numbers 6,7,9,10,11-19,22,24 in the wavelength regions of 783,782,777,677 cm^{-1}. In 777 cm^{-1} wavelength regions this mineral Si-O symmetric bending vibration [1]-[12],[?],[?] reveals in all site numbers 1-25. In site numbers 12,18 and 21 the Quartz mineral is available with Si-O-Si asymmetrical bending vibration in wavelength regions of 514,464 and 458 cm^{-1}. At the site locations of 9,16,17,24 with band vibration of Si-O bending vibrational bands the quartz mineral obtained at the wavenumber region of 434, 433 cm^{-1}.

3.1.2. ***Feldspar (Orthoclase, Microcline, Albite) (X)[$AlSiO_3O_8$]***

Feldspar's general chemical formula is (X)[$AlSiO_3O_8$], where X stands for K, Na or Ca Potassium Aluminium Silicate, Sodium Aluminium Silicate and Calcium Aluminium Silicate. Orthoclase, Microline, Anorthoclase, Albite etc are included in the group of Feldspar minerals. In the Pachamalai hills, Feldspar minerals are available in rich amounts in almost all the site numbers in various locations. 1790,639, 535 cm^{-1} wavelength regions Al-O Co-ordination vibrations show the Feldspar minerals present in rich amounts at the site numbers 7,21. At 586-582 cm^{-1} wavelength region O-Si(Al)-O bending vibration [1]-[8],[13],[19] revealed at site numbers 6-18,21-24.

3.1.3. *Clay Minerals (Kaolinite, Montmorillonite, Illite)*

Kaolinite is a necessary clay mineral with chemical formula $Al_4Si_4O_{10}(OH_8)$ available in almost all site locations. In wavenumber 3695 cm^{-1} with Plane declined vibration of H_2O band Kaolinite revealed only at site number 25. At the site location of 4 and 5 with OH elongation mode [6],[7],[8] this mineral is revealed at wavenumber 3693 cm^{-1}, with symmetric elongation vibration band this mineral presents 3418 cm^{-1} at the location numbers 16, 17 and 18. 1-5,10,12-16,23,24 site locations with the wavenumber region of 1036 -1028 cm^{-1} kaolinite mineral shows their presence with band absorption of Si-O stretching.

Montmorillonite is another important clay mineral which is available randomly in all site locations, its chemical formula is $(Na,Ca)_{0.3}(Al,Mg)_2Si_4\ O_{10}(OH)_2\ nH_2O$. At the site locations 3, 25 this mineral shows their presence with OH band vibration in wavenumber region of 3620 cm^{-1}. In the wavenumber region of 3441 – 3431 cm^{-1} band vibration of H–O–H stretching of water molecules [12],[13] this mineral is available at the locations of 3,12,15 and 24. At the site locations 1 and 17 the Montmorillonite mineral shows its presence with a wavenumber of 3426 cm^{-1} and 1025 cm^{-1} with H–O–H stretching of water molecules' vibrational band respectively. In wavenumber of 911 & 910 cm^{-1} this mineral shows their presence at the site locations of 4, 5, 25 with vibration band of MVI-OH low-precision deflection vibration.

Illite is the clay mineral with chemical constitution of $(K,H_3O)(Al,Mg,Fe)_2\ (Si,Al)_4O_{10}(OH)_2,(H_2O)$ revealed at the site locations of 1-6,9,11-18,22-25 with the vibration band of H–O–H stretching in the wavenumber region of 1637 - 1627 cm^{-1} [20],[17],[12].

3.1.4. *Carbonate Minerals (Calcite, Aragonite, Dolomite)*

Calcite is an important carbonate mineral calcium carbonate $CaCO_3$ is available in almost all the site locations. With band vibration of $CaCO_3$ asymmetrical bending calcite revealed in the site numbers of 1-5,8-12,16,17,22-24 at the wavenumber of 1384 and 1383 cm^{-1} [11],[16].

3.1.5. *Magnetic Minerals (Hematite,Magnetite, Geothite)*

Hematite is essential magnetic mineral with chemical formula Fe_2O_3 shows their presence in maximum site numbers 3-13,15-18,22-25 with vibration of various chemical elements like C-X [X=Cl, Br, I] band at the wavenumber region of 540-536 cm^{-1}. In the site numbers of 8,20 the hematite mineral revealed Si–O–Al band vibration with the wavenumber region of 524-520 cm^{-1} [16],[20],[17],[12].

Fe_3O_4 chemical composition is the Magnetite mineral is another important magnetic material that shows their availability with wavenumber of 575 cm^{-1} at the site number of 2. Similarly Geothite with chmical formula α-Fe(OH)O revealed at site number 21 with the wavenumber of 459 cm^{-1}.

3.1.6. Other Minerals

Organic Carbon randomly oriented in the rock samples in all locations of hills, this shows their presence at the wavenumber region of 2855 – 2853 cm^{-1} and 2924 cm-1 in the site locations of 5,14,15,25 and 1-3,6,9-12,20,25 repectively.

Diopside is a monoclinic pyroxene mineral with composition $CaMgSi_2O_6$ obtained at the wavenumber region of 634 – 630 cm^{-1} with band vibration of S-O-Si bending[16] in the site locations of 1,2,6-9,11-13,16,17,22-24. Hectorite is a rare soft, greasy white clay mineral with chemical constitution of $Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2$ shows their presence at the frequency range of 1013 – 1011cm^{-1} with Si-O stretching band in the site locations of 1,9,13,18.

Chrysotile is a serpentine silicate mineral, with chemical formula $Mg_3Si_2O_5(OH)_4$ revealed at 3694 cm^{-1} frequency range with OH stretching region[(?)] at the site number 3. Smectites is mixture of various swelling sheet silicate with have three layers, its chemical composition is $M_{0.33}{}^{+}Al_2(Si_{3.67}Al_{0.33})O_{10}\ (OH)_2$ M^+ represents exchangeable cations like Ca^{2+} and Mg^{2+} shows their presence at frequency 3430 cm^{-1} with band vibration of H-O-H stretching vibration at the site number 6.

Wollastonite is a calcium inosilicate mineral (CaSiO3) that may contain small amounts of iron, magnesium, and manganese substituting for calcium shows their presence at frequency ranges at 1080 -1079 with Si-O-Si absorption at the site locations of 8,20,21. Saponite is a trioctahedral mineral of the smectite group. Its chemical formula is $(Na,Ca)_{0.25}Mg_3(Si,Al)_4O_{10}(OH)_2.4H_2O$ available in frequency range at 1010 cm^{-1} with band absorption of Si-O stretching band[10],[11],[16],[20] at site numbers 22,25. Anorthite mineral revealed with chemical composition of $CaAl_2Si_2O_8$ with the frequency range of 753 &752 cm^{-1} with band absorption of Si-Al(Si) stretching mode at the site location of 4,5.

3.2 Crystallinity Index and Nature of Crystallinity

The Crystallinity Index could be defined as the fraction of crystalline materials in a mixture of crystalline and non-crystalline materials. It cannot be found directly and is determined from the crystallinity index which is inversely proportional to crystallinity. Quartz is the major mineral present in all the sediment samples, the crystallinity index could be found.

If crystallinity is minimum, then the minerals are said to be disordered. If it is maximum, then the minerals are considered to be ordered state[15]. The Ratio of absorption band around 777 cm^{-1} (I_{777}) and 695 cm^{-1} (I_{695}) are taken to calculate the crystallinity index of the minerals. When the crystallinity index is minimum, the minerals are said to be well crystallized and if it is maximum, the minerals are considered to be in a poorly crystallized state[15]. In Pachamalai hills the Nature of crystallinity shows the random manner.

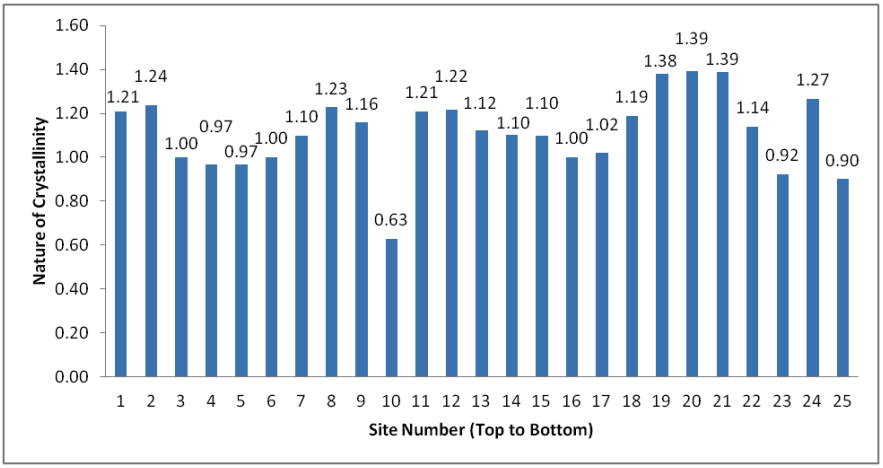

Fig 4. Nature of Crystallinity of Pachamalai Hills from Top to Bottom (1-25) locations

3.3 X-Ray Diffraction Analysis

The XRD is employed to determine the different mineral phases present in the rock samples. Minerals were identified using different peaks with 2θ position and d-spacing values, their corresponding (hkl) values utilized to study the crystalline structure of the minerals as well. In Pachamalai hills all site locations from 1 to 25 were carried out to evaluate the presence of minerals. Figure **??** shows the various minerals available in the site number 12, Table 2 represents the minerals revealed in the same site number. The comparison of XRD spectra is depicted in Figure **??** for all 25 locations. In site number 12 diffraction peaks at 2θ position values 39.84°, 40.51°, 55.12°, 68.50° and 73.78° with the corresponding d-spacing values 2.2625 Å, 2.2267 Å, 1.6660 Å, 1.3697 Å, 1.2842 Å and (hkl) values are (112) (113) (112) (031) (104) are shows the presence of hexagonal shape Quartz mineral according to JCPDS (N 00-046-1045)[1]. However, the peaks observed at 2θ: 28.03°, 28.26°, 38.03° corresponds to crystalline plane (021) (021) (031) with the d-spacing values 3.1832 Å, 3.1570 Å, 2.3658 Å belong to Kaolinite mineral[6],[9],[17].

The diffraction peaks at 2θ: 23.89°, 36.55°, 46.01° and 26.93°, 60.20°, 62.56° and their corresponding d-spacing values 3.7245 Å, 2.4584 Å, 1.9725 Å and 3.3104 Å, 1.5371 Å, 1.4847 Å with the crystalline phase values of (hkl) are (131) (240) (333) and (002) (510) (481) are support the occurrence of Microline Feldspar and Orthoclase Feldspar respectively[4],[8],[16]. Albite minerals were confirming their presents at significant reflections in the position of 2θ: 23.18°, 47.64°, 51.04° with suitable d-spacing values 3.8371, 1.9085, 1.7891 and the crystalline planes (111) (352) (331). Similarly, the deflection position 2θ: 21.10 °, 22.25°, 35.76° and 25.81, 42.77 with suitable d-spacing values 4.2099 Å, 3.9952 Å, 2.5104 Å and 3.4506 Å, 2.1138 Å and the crystalline structure (020) (020) (011) and (111) (121) belong to Goethite, Aragonite and Calcite respectively[17]-[13].

The essential minerals like Zircon, Monazite and Magnetite were showing their occurrence in the position of 2θ: 3.69°, 31.25°, 31.71°, 50.34° and 64.13° with suitable d-spacing values 2.9131 Å, 2.8616 Å, 2.8215 Å, 1.8125 Å and 1.4520 Å with the crystalline phases (402) (200) (200) (354) and (140).

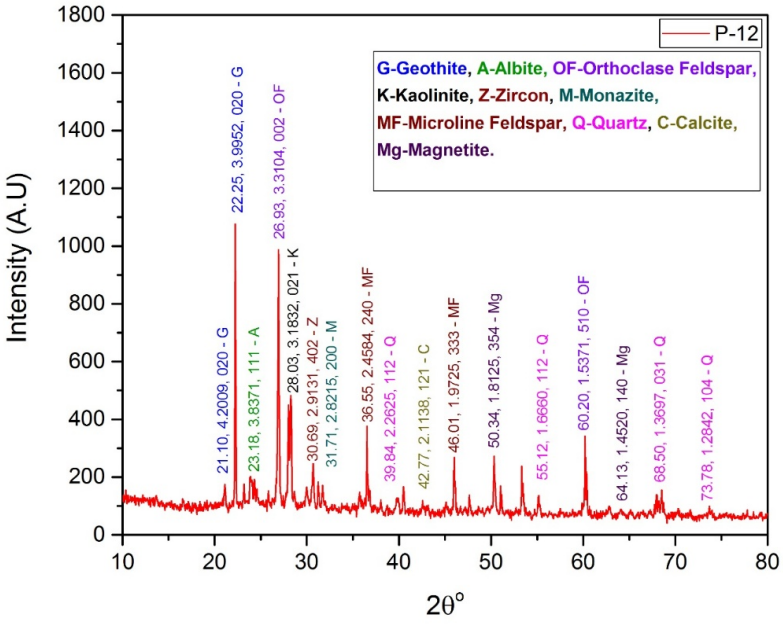

Fig 5. XRD Spectrum of Pachamalai Hills at site number 12

The diffraction peaks at 2θ: 23.89°, 36.55°, 46.01° and 26.93°, 60.20°, 62.56° and their corresponding d-spacing values 3.7245 Å, 2.4584 Å, 1.9725 Å and 3.3104 Å, 1.5371 Å, 1.4847 Å with the crystalline phase values of (hkl) are (131) (240) (333) and (002) (510) (481) are support the occurrence of Microline Feldspar and Orthoclase Feldspar respectively. Albite minerals were confirming their presents at significant reflections in the position of 2θ: 23.18°, 47.64°, 51.04° with suitable d-spacing values 3.8371, 1.9085, 1.7891 and the crystalline planes (111) (352) (331)[19],[?]. Similarly, the deflection position 2θ: 21.10 °, 22.25°,

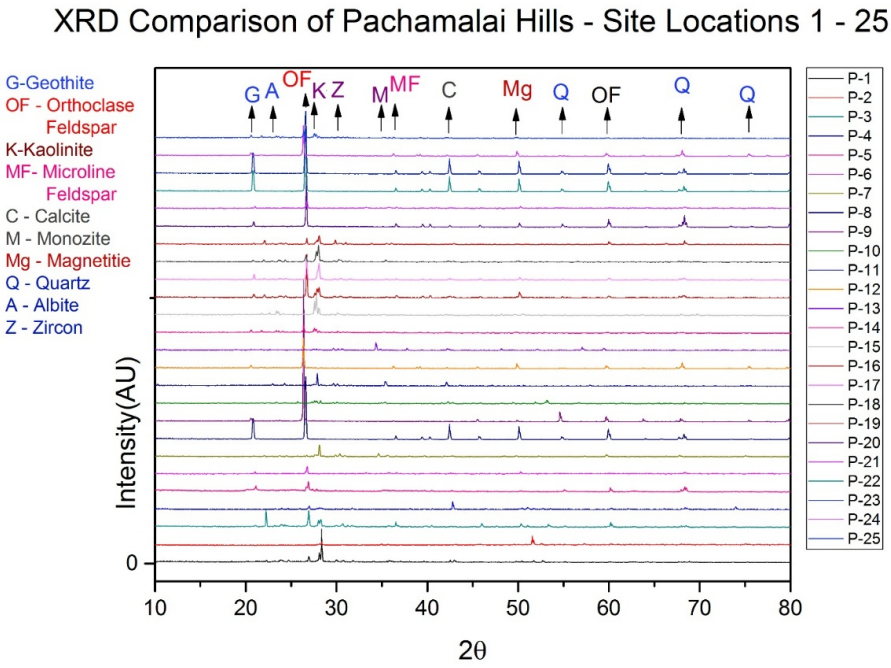

Fig 6. XRD Analysis of Pachamalai Hills - site numbers 1to 25

35.76° and 25.81, 42.77 with suitable d-spacing values 4.2099 Å, 3.9952 Å, 2.5104 Å and 3.4506 Å, 2.1138 Å and the crystalline structure (020) (020) (011) and (111) (121) belong to Goethite, Aragonite and Calcite respectively.

The essential minerals like Zircon, Monazite and Magnetite were showing their occurrence in the position of 2θ: 3.69°, 31.25°, 31.71°, 50.34° and 64.13° with suitable d-spacing values 2.9131 Å, 2.8616 Å, 2.8215 Å, 1.8125 Å and 1.4520 Å with the crystalline phases (402) (200) (200) (354) and (140).

3.4 EDX with SEM

The EDX with SEM investigations are beneficial for determining the surface structure, internal morphology and superficial elemental profile[7],[?]. The energy-dispersive X-ray spectroscopy analysis for Pachamalai hills rock powdered samples shown in Figure 7. Its elements along with their atomic weight percentage are given in Table 3. In SEM (Scanning Electron Microscope) images show the grain size which is poorly sorted and appear in a variety of shapes and sizes ranging from 50-70 mm[4],[6],[7],[8]. The EDX results display that Oxygen, Carbon and Silicon elements are the significant components across the five samples. The Quartz (SiO_2) mineral is the most predominant mineral in the investigated samples in almost all sites. From the five selected locations the silicon element reveals 10.27 % to 24.38% with mean value of 17.05%. The Aluminium element is the next mineral that shows their domination in site number 9 has atomic percentage 9.96% as maximum in site number 9 and minimum in 0.93% at site location 14, from all selected 5 locations it shows the average value is 5.57%. The most important element for the industrial applications the Iron element present 0.58% to 3.65% with mean value of 2.43% in five site locations. The rare earth material Titanium present in these hills, at site numbers 5, 20 and 25. its availability reveals 0.21% as maximum value, and its mean value is 0.17%. Similarly other essential minerals Sodium (1.32%), Magnesium (1.63%), Sulphur (0.14%), Potassium 0.35%, Calcium 2.68% and Copper 0.18% has shown their significant mean presence in the five mentioned site numbers of the hill. The examined elements are accomplished with FTIR and XRD results.

The high content of Silicon along with calcium indicates the presence of sand as a siliceous aggregate which was verified by disaggregation of the material[10]. The samples magnesium, aluminium, potassium and titanium probably indicate the presence of clay in these samples has good agreement with FTIR and XRD results. The iron element expressive percentage (3.65% and 0.17%) shows the presence of Ferrous oxide compounds; in FTIR and XRD spectra it explains the availability of Magnetite, Hematite and Feldspar minerals.

Table 2. XRD Spectrum analysis of Pachamalai Hills – Site No 12

S. No	Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	h k l	Mineral Name
1	21.1036	80.51	0.1181	4.20991	8.35	020	Goethite
2	22.2515	964.61	0.1181	3.99526	100	020	Goethite
3	23.181	86.85	0.1181	3.83712	9	111	Albite
4	23.8915	109.33	0.1181	3.72459	11.33	131	Microline Feldspar
5	25.8198	53.58	0.1181	3.45064	5.55	111	Aragonite
6	26.9331	931.12	0.1181	3.31048	96.53	002	Orthoclase Feldspar
7	28.0313	322.3	0.1181	3.18323	33.41	021	Kaolinite
8	28.2689	394.11	0.1181	3.15702	40.86	021	Kaolinite
9	30.6916	157.19	0.1574	2.91311	16.3	402	Zircon
10	31.2579	89.89	0.1181	2.86161	9.32	200	Monazite
11	31.7135	83.62	0.1574	2.82154	8.67	200	Monazite
12	35.7685	46.51	0.2362	2.51042	4.82	011	Goethite
13	36.5517	160.66	0.1181	2.45841	16.66	240	Microline Feldspar
14	38.0357	25.89	0.2362	2.36583	2.68	031	Kaolinite
15	39.843	42.85	0.3149	2.26259	4.44	112	Quartz
16	40.5116	84.66	0.1574	2.22678	8.78	113	Quartz
17	42.7782	9.6	0.4723	2.11389	1	121	Cacite
18	46.0121	184.15	0.1968	1.97257	19.09	333	Microline Feldspar
19	47.6486	58.62	0.1574	1.90858	6.08	352	Albite
20	50.3437	168.44	0.1181	1.81254	17.46	354	Magnetite
21	51.0497	87.86	0.1574	1.78912	9.11	331	Albite
22	55.126	59.22	0.1181	1.66609	6.14	112	Quartz
23	60.2023	274.23	0.0787	1.53718	28.43	510	Orthoclase Feldspar
24	62.5601	12.1	0.6298	1.48479	1.25	481	Orthoclase Feldspar
25	64.1358	15.64	0.4723	1.45207	1.62	140	Magnetite
26	68.5056	90.03	0.1181	1.36971	9.33	031	Quartz
27	73.7803	18.57	0.4723	1.28429	1.93	104	Quartz

Table 3. Element Identification of Pachamalai Hills using EDX at Site numbers 9 and 25

Element	Site No-05		Site No-09		Site No-14		Site No-20		Site No-25		Mean	
Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	
C	23.98	33.64	22.88	30.95	20.47	28.72	5.97	9.59	13.47	20.09	17.35	24.60
O	48.5	51.09	55.98	56.84	52.59	55.39	54.2	65.32	53.04	59.38	52.86	57.60
Na	1.73	1.27	*	*	0.25	0.19	1.21	1.01	2.09	1.63	1.32	1.03
Mg	1.47	1.02	*	*	*	*	2.9	2.3	0.52	0.38	1.63	1.23
Al	4.62	2.89	9.96	6.00	0.93	0.58	7.25	5.18	5.1	3.39	5.57	3.61
Si	12.52	7.51	10.27	5.94	24.38	14.63	17.37	11.93	20.69	13.19	17.05	10.64
S	0.14	0.08	*	*	*	*	*	*	*	*	0.14	0.08
K	0.37	0.16	0.17	0.07	0.5	0.22	0.24	0.12	0.47	0.21	0.35	0.16
Ca	2.8	1.18	*	*	0.16	0.07	5.88	2.83	1.87	0.84	2.68	1.23
Ti	0.21	0.07	*	*	*	*	0.19	0.08	0.12	0.04	0.17	0.06
Fe	3.65	1.1	0.58	0.17	0.72	0.22	4.8	1.66	2.42	0.78	2.43	0.79
Cu	*	*	0.15	0.04	*	*	*	*	0.21	0.06	0.18	0.05
Totals	**100**		**100**		**100**		**100**		**100**			

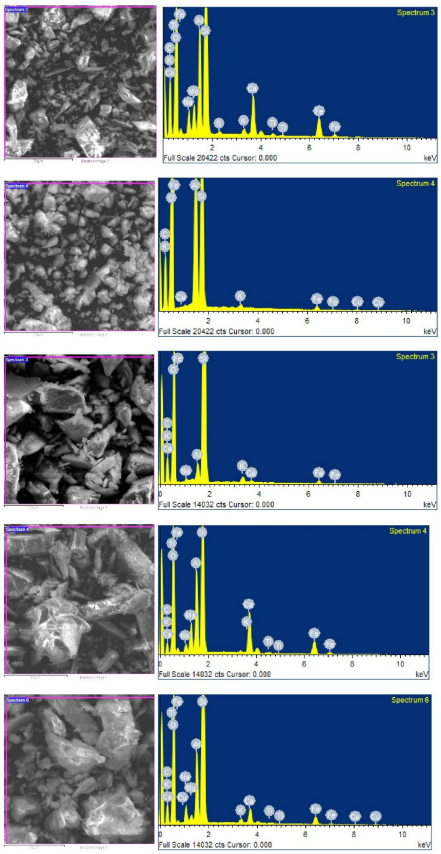

Fig 7. EDX with SEM images of Pachamalai hills site Numbers 9 and 25

3.5 XPS

XPS provides quantification of elemental and chemical composition at an information depth of 5-10 nm from the surface. The sensitivity of SPS allows it to determine functionalities and oxidation states of elements and to detect small differences between the samples. This ability of the XPS provides us to understand the surface chemistry of the rocks in more detail[14]. Figure 9 shows the survey spectrum revealed from Pachamalai hills at site number 17. XPS has the ability to detect the oxygen, carbon, silicon, iron, Magnesium, calcium, potassium and sulphur with their functionalities and oxidation. Such ability of XPS provides opportunities to understand the surface chemistry of the rocks, and it is a suitable technique for elucidating the mechanism of chemical weathering of minerals[14],[19],[18].

X-ray photoelectron spectroscopy measurements were carried out with a Perkin-Elmer PHI 5400 spectrometer. A twin anode X-ray source was utilised with Mg Ka X-rays (hn = 1253.6 eV). A series of wide scan survey spectra were collected using analyser pass energy of 89.45 eV and a step size of 0.5 eV. The electron take-off angle was 45, and the power of the X-ray source was 200W. The powder samples were mounted on a conductive carbon tape[18].

During XPS measurements, both X-ray and flood gun electron irradiation produces a net charge on the sample with a consequent shift in binding energies (E_b)[18]. This shift must be corrected during analysis using a reference signal to achieve a proper adjudication of constituent spices to the signal. The standard procedure involves energy correction based on C1s peak, considering this signal comes from adventitious carbon with an aliphatic nature and characteristic signal at 312 eV, with the atomic percentage of 24.1%. The calibration of Oxygen O-KLL and O-1s have the binding energy characteristic peak at 956 eV and 531 eV respectively with the atomic percentage of 58.2%. The narrow spectra of the sample P-17 show the characteristic signal at 785 eV, 724eV and 713eV for Iron element Fe LMM, Fe 2p1and 2ps respectively.

Due to proximity of binding energy between 350 eV – 361 eV and 462 eV the normal presence of Calcium element in the characteristic peaks' electronic configuration of Ca-2s, Ca-2p, Ca-2p1 and Ca-2p3. It can be noted that the experimental data can be fitted by convolution of four peaks of K (Potassium) assigned the binding energy at 401 eV, 310 eV, 309 eV and 288 eV characteristic peaks with K-2s, K-2p, K-2p1 and K-2p3 electronic configurations. The maximum signals of Silicon elements

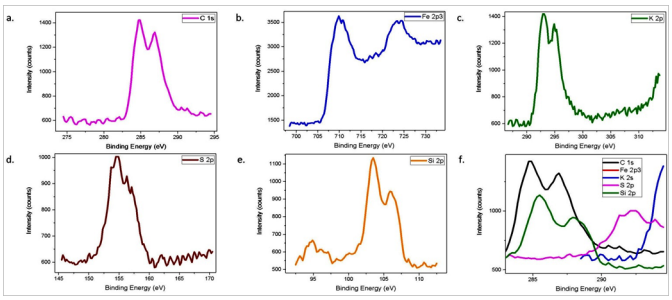

Fig 8. The element spectra of a. C 1s, b. Fe 2p3, c. K 2p, d. S 2p, e. Si 2p, f. The comparison the elements (C, Fe, K, S and Si)

2p and 2s present in the characteristic peaks at 165 eV and 112 eV. The sulphur elements in the region of 201-197 eV binding energy confirm the electronic configuration of S-2p and S-2s. The salt mineral Magnetism revealed in the characteristic signals 234 eV, 101 eV and 92 eV confirm their availability with the electronic configuration of Mg-KLL, Mg-2p and Mg-2s.

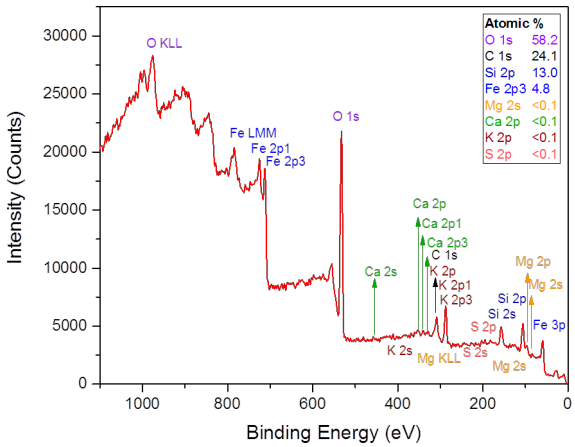

Fig 9. The XPS spectrum of Pachamalai Hills at site number P-17

4 Conclusion

The sedimentary rock samples of Pachamalai hills powdered rock samples were analysed by spectroscopic techniques such as FTIR, XRD, EDX with SEM and XPS in order to study the contribution and acquisition of morphological, chemical and mineralogical information.

In FTIR studies Quartz, Calcite, Cristobalite, Gibbsite, Goethite, Halloysite, Hectorite, Illite, Kaolinite, Lepidocrocite, Microcline Feldspar, Montmorillonite, Nacrite, Organic Compound, Palygorskite, Sepiolite, and Siderite minerals were identified. According to FTIR results most functional groups represents the Quartz (SiO_2), and some vibration mode confirms the Kaolinite and Feldspar as the major minerals in these hills.

From XRD analysis these minerals' presence were confirmed and some additional minerals also identified like Zircon, Monazite, Aragonite and Magnetite. Their crystalline morphology hkl values were tabulated. But some minerals like Saponite, Smectites and Diopside are could not reveal due to their poor crystalline nature. The nature of crystallinity of the materials (0.63 to 1.39) has shown the randomly varying values, showing the nonuniform crystalline posed by the hills from elevation wise. But among the 25 examined locations 20 locations has shown the nature of crystanillity range from 1.0 to 1.39 exhibits the high crystalline nature.

EDX with SEM images utilized for elemental analysis and their grain boundaries. In this study the important metals like Al, Fe, Cu and Ti are occupied the major constitution in these hills. Among these Aluminium has shown the maximum presence 4.62% and Cupper is 0.15 % as minimum. The non-metal elements like Na, Mg, S, K, Si and Ca are posses' good numbers in atomic weight percentages, here Si -12.5% as maximum and S – 0.14% as minimum occupancy in these hills.

The XPS has generally been used to determine the surface chemical composition of the rock samples revealed like various elements like oxygen, carbon, silicon, iron, Magnesium, calcium, potassium and sulphur, and these studies carried out for study of functionalities and oxidation states of elements. The Fe has shown its maximum obtained mineral in the atomic percentage of 4.8%. The other elements Mg, Ca, K and S has shown their occupancy less than 1% according to their chemical composition.

References

1) Hachem R, Meftah N, Bouaziz A. A comparative analysis of the microstructural and physicochemical properties of alluvial and dune sands from northeast Algerian Sahara. *The Journal of Engineering and Exact Sciences – jCEC*. 2023;9(6). https://doi.org/10.18540/jcecvl9iss6pp16222-01e.
2) Jozanikohan G, Abarghooei MN. The Fourier transform infrared spectroscopy (FTIR) analysis for the clay mineralogy studies in a clastic reservoir. *Journal of Petroleum Exploration and Production Technology*. 2022;12:2093–2106. https://doi.org/10.1007/s13202-021-01449-y.
3) Iranfar S, Karbala MM, Shakiba M, Shahsavari MH. Effects of type and distribution of clay minerals on the physicochemical and geomechanical properties of engineered porous rocks. *Scientific Reports*. 2023;13:5837. https://doi.org/10.1038/s41598-023-33103-4.
4) Zoungrana JB, Sorgho B, Bakouan C, Sawadogo S, Ouedraogo RD, e Guel B, et al. Mineralogical study of phosphate rocks by quantitative rietveld refinement. *Open Ceramics*. 2024;18:100567. https://doi.org/10.1016/j.oceram.2024.100567.
5) Paramasivam R, Shanmugam S, Venkidasamy R, Shanmugam A. Mineralogical Characterization Of Sediments, Kalrayan Hills South India - A FTIR Study. *Journal of Advanced Scientific Research*. 2021;12(1):66–74. https://doi.org/10.55218/JASR.202112109.
6) Nicoli M, Eftekhari N, Vaccaro C, Giraldo HC, Garcês S, Gomes H, et al. A multi-analytical evaluation of the depositional pattern on open-air rock art panels at "Abrigo del Lince" (Badajoz, Spain). *Environmental Science and Pollution Research*. 2023;30:24344–24360. https://doi.org/10.1007/s11356-022-23589-2.
7) Rahman MS, Metselaar HSC, Razak BBA. Mineralogical and Thermal Analysis of Ancient Ceramic Artifacts Based on Modern Techniques of Ceramic Studies. *Mediterranean Archaeology and Archaeometry*. 2024;24(3):1131. https://doi.org/10.5281/zenodo.13383260.
8) Seetha D, Velraj G. FT-IR, XRD, SEM-EDS, EDXRF and chemometric analyses of archaeological artifacts recently excavated from Chandravalli in Karnataka State, South India. *Radiation Physics and Chemistry*. 2019;162:114–120. https://doi.org/10.1016/j.radphyschem.2019.03.017.
9) Papakosta V, Lopez-Costas O, Isaksson S. Multi-Method (Ftir, Xrd, Pxrf) Analysis Of Ertebølle Pottery Ceramics From Scania, Southern Sweden. *Archaeometry*. 2020;62(4):677–693. https://doi.org/10.1111/arcm.12554.
10) SEISEH R, MAYYAS A, AL-SABABHA H, SEKHENEH WA, POPP J. FTIR and Thermogravimetric Analysis of Ancient Mortar from Al-Amuwaqqar Early Islamic Bathhouse in Jordan for Conservation use. *International Journal Of Conservation Science*. 2023;14(1):3–18. https://doi.org/10.36868/IJCS.2023.01.01.
11) Bayazit M, Kaynak E, Coşkun N. Chemical And Mineralogical Analyses Of The Late Neolithic Ceramics From Şah Valley (Singuber), Turkey. *Journal of Scientific Reports – A*. 2023. https://doi.org/10.59313/jsr-a.1206576.
12) Ibrahim MBA, Yao KA, Digbehi ZB. Mineralogical characterization of Upper Cretaceous petroleum source rocks of Termit sedimentary basin (Niger). *Journal of Materials and Environmental Science*. 2020;11:1173–1183.
13) Reethu M, Jyothi V, Sandeep K, Rafaz AK, Aravind GH, Jithin J. Rock Magnetic and Mineralogical Properties of Lateritic Soil Profiles Developed on Two Different Parent Rocks in Northern Kerala, South-Western India. *Journal of Geoscience Research*. 2023;8(2):110–117. https://doi.org/10.56153/g19088-022-0131-30.
14) Murugesu MP, Prasad M, Pylypenk S. Surface and bulk characterization of reservoir and cap-rocks: Past, present, and future. *Journal of Vacuum science and technology A*. 2020;38:050801. https://doi.org/10.1116/6.0000319.
15) Mullainathan S, Nithiyanantham S. FTIR spectroscopic studies of rock sediments in Namakkal, Tamil Nadu, South India, for vegetations. *Environ Earth Sci*. 2016;75:692. https://doi.org/10.1007/s12665-016-5384-0.
16) Lorna C, Peter OO, Moses RK. Multi-analytical Approach (FTIR, XRF, XRD, GC-MS) Characterization of Source Rocks from the Anza Basin, Kenya. *Mediterranean Journal of Chemistry*. 2023;13(2):145–155. https://doi.org/10.13171/mjc023040171687chesir.
17) Patra B, Pal R, Paulraj R, Pradhan SN, Meena R. Mineralogical composition and C/N contents in soil and water among betel vineyards of coastal Odisha, India. *SN Applied Sciences*. 2020;2:998. https://doi.org/10.1007/s42452-020-2631-5.
18) Donadelli JA, Cánneva A, Erra G, Calvo A. XPS direct analysis on shale rocks: Correlation with kerogen type and Maturity. *Fuel*. 2019;257:116004. https://doi.org/10.1016/j.fuel.2019.116004.
19) Ayoubi S, Adman V. Iron Mineralogy and Magnetic Susceptibility of Soils Developed On Various Rocks In Western Iran. *Clays And Clay Minerals*. 2019;67(3):217–227. https://doi.org/10.1007/S42860-019-00020-5.
20) Plessis PID, Gazley MF, Tay SL, Trunfull EF, Knorsch M, Branch T, et al. Quantification of Kaolinite and Halloysite Using Machine Learning from FTIR, XRF, and Brightness Data. *Minerals*. 2021;11:1350. https://doi.org/10.3390/min11121350.