Baseline Study of Rock Samples Collected From Paleolithic Archaeological Site of Attirampakkam, Tamil Nadu

A Tamilarasi (tamilarasia@ssn.edu.in)
SSN College of Engineering, Kalavakkam, Chennai.

A Chandrasekaran
SSN College of Engineering, Kalavakkam, Chennai.

V Sathish
SSN College of Engineering, Kalavakkam, Chennai.

Manigandan S
SSN College of Engineering, Kalavakkam, Chennai.

Lakshmi A
SSN College of Engineering, Kalavakkam, Chennai.

Research Article

Keywords: Rock, Paleolithic archaeological site, FT-IR, crystallinity index, XRD

DOI: https://doi.org/10.21203/rs.3.rs-759784/v1

License: ©  This work is licensed under a Creative Commons Attribution 4.0 International License.
Abstract

In the present work, rock samples have been collected from Paleolithic archaeological site Attirampakkam, Tamil Nadu, India to assess the presence of mineralogical composition of samples using Fourier Transform infrared-spectroscopic (FT-IR) technique and these identified minerals are confirmed by using X-Ray Diffraction (XRD) technique. From FT-IR spectra the presence of minerals such as quartz, orthoclase, microcline, kaolinite, montmorillonite, dolomite, aragonite, and palygrosite minerals are identified in rock samples. In this samples quartz is the majorly presented mineral and crystallinity index of quartz \( (\text{SiO}_2) \) is estimated for all the samples by comparing the ratio of intensity of the characteristic peak at 778 and 695 cm\(^{-1}\) with the corresponding ratio for a standard sample. In rock samples, calculated crystallinity index of quartz is greater than 1 and shows that the disordered in nature. Additionally some more minerals such as hematite and rutile are identified in rock samples by X-ray diffraction technique. This extensive study shows that the archeological rock samples are wide variation in mineral composition.

1. Introduction

The crust of Earth is aggregated with different types of rocks. Rocks are made up of one or more minerals. These minerals are well known as rock-forming minerals. The Earth's crust is fully made up of minerals. Rocks and minerals are all around us, it plays a valuable role in the natural system. Naturally, rocks are classified into three types, according to how they formed such as (i) Igneous rocks, (ii) Sedimentary rock, (iii) Metamorphic rocks (Ravisankar et al., 2012). Igneous rocks are formed from the cooling and solidification of lava or magma. The sedimentary rocks are formed when compaction and cementation of the sediments. When the rocks are changed as a result of exposure to intense heat and or pressure is well known as metamorphic rocks.

Dwellings of humans are made up of stone even travel to work on stone-paved roads. The archaeological study of rock is crucial for discovering human heritage because the stone has accompanied humans for millions of years, not only as a construction material, but also as a medium for the fabrication of tools, cult items, and jewelry (Szczepaniak, 2014). Much other evidence of previous civilizations (such as organic matters or oral tradition) degrade and are destroyed, therefore archaeological records are exceptionally rich in evidence of stone working products. A critical analysis of these artefacts, incorporating determination of materials, manufacturing techniques, and rock metamorphosis throughout time, would serve in tracing the modalities of interaction between human civilizations and geological resources (Sciuto, 2018). Minerals and stones are also used as medicine in ancient periods (Wasilewski, 2009). The mineralogical composition of rock samples done by using Fourier transforms Infrared Spectroscopy (FT-IR). To obtain both the chemical and mineralogical composition of archaeological materials FT-IR is an efficient tool (Saravanan et al., 2013). X-Ray diffraction (XRD) used to determine the rock sample's chemical compositions that are in crystalline nature. In the present work, the main objectives are to (i) identify the major and minor minerals present in the rock samples by FT-IR technique (ii) find the crystallinity index of the quartz and (ii) confirm the minerals by XRD technique.

2. Geology Of Study Area

Attirampakkam (13.2322°N and 79.8801°E) is an open-air Paleolithic archaeological site located on the southeastern coast of India on 1 km to the north of the tributary of kortallaiyar in Tamil Nadu, (Fig: 1). The village where the oldest known stone tools found in India became the site of a type of Madras culture. The first well-shaped oval type stone tool was identified by Robert Bruce Foote and his colleague William King when they investigated the on 28th September 1863 near sriperumbudur shale beds around to the Attirampakkam (Foote, 1865). It is the oldest Paleolithic Archaeological site in India is dated back to 1.7 million years. But any fossils remains of hominid groups is haven't found on this site. Many archaeological sites in India hominines group fossil remains are found such as Hothenora, Bhimbetka, Adamgarh and Tikoda in Madhya Pradesh as well as Kuliana in Odisha. But more than all of these excavation sites Attirampakkam is one of the oldest Acheulian site in India which was compared to earliest prehistoric antiquity such as, Africa, China, and Europe (Chauhan, 2009).

The sampling site Attirampakkam is located in the kortallaiyar river basin, Tamilnadu, is well known as a lower and middle Paleolithic site in India (Foote, 1865). In 1863 this site was discovered by British geologist Robert Bruce Foote (Pappu, 2001). A comprehensive investigation of this site was continued for over a century. Excavations are well preserved primarily revealing a multicultural base with lower, middle and upper Paleolithic deposits circumstances (Pappu, 2003).
3. Materials

3.2. Rock sample collection

With this site 10 rock specimens of different shapes and structures have been collected and packed in polythene bags. These samples were named as AR-1, AR-2, AR-3, AR-4, AR-5, AR-6, AR-7, AR-8, AR-9 and AR-10. The sampling area was located in the tributary stream of the Kortallaiyar river basin (Pappu, 2007). The atmospheric layer of each sample was cleaned and then removed in the laboratory. The remaining sample was crushed for this investigation of this study. Agate motor was used to grain the sample, and these grain powders were sieved using a 63μm mesh screen, and all the particles were the same size. To remove the moisture content of grained powder samples were dried by using hot air oven at 110°C.

3.3. Sample Preparation for FT-IR

In this trial, KBr compressed-pellet techniques were used to prepare a sample for the FT-IR technique. In this preparation, 2 mg of powder rock sample was mixed with the 40 mg of KBr in a 1:20 ratio using mortar and pestle (Ramasamy et al., 2005). Before this process the potassium bromide was well grained and dried at 120°C in hot air oven. Laboratory hydraulic press was used to create the pressure in the sample and KBr powder mixer for making pellets. Similar procedure were done by all samples for this technique. Before being put within an appropriate sample holder and applied for the measurement of the infrared beams, the created pellets were kept in a moisture-free container.

3.4 Sample Preparation for XRD

A tiny fragment of material weighing about 0.2g was ground manually using an agate mortar for X-ray diffraction investigation. These powdered samples are stored in plastic vials. Each samples are packaged in a homogenous process for this investigation. In the study the samples are subjected to the sample holder of the X-ray diffractometer.

4. Methods

4.2. FT-IR analysis

The qualitative determination of major and minor minerals in the samples was done by using FT-IR techniques. The identification of minerals in rock samples is one of the most valuable and essential applications of infrared spectroscopy investigations (Mullainathan and Nithiyanantham, 2016). Each sample pellets prepared by the same procedure and the spectra were recorded in the mid-range 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). To the analysis of minerals, infrared spectrum in the range 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) is important (Ikhane, 2020; White and Roth, 1996; Karr, 2013). By comparing pure as well as synthetic mineral values in the literature, the minerals are described based on band position or peak locations. The sharpness or diffuseness of bands, in order to band orientations, may contribute to mineral component identification.

4.3. XRD analysis

The XRD analysis was used for the structure analysis of the samples such as identification of phases, accuracy in unit cell determination, and measurement of particle size analysis. XRD technique is quick and accurate method to identifying the crystal structure and mineral phases (Mullainathan and Nithiyanantham, 2013). X-ray diffractometer has three component such as an X-ray tube, a sample holder, and an x-ray detector (Connolly, 2007). The powdered sample was homogeneously spread over an aluminum holder that acted as a sample container in the X-ray diffractometer. The XRD powder pattern of each samples were recorded at ambient temperature. X-ray diffraction peaks are formed by the creative interference of a monochromatic beam of X-rays scattering with specific angles from each lattice planes of the sample (Bunaciu, 2015).

5. Results And Discussion

5.2. Minerals In rock samples
Figure 1 shows the infrared spectra of the rock samples in the frequency range 400-4000 cm\(^{-1}\). The minerals such as quartz, orthoclase feldspar, microcline feldspar, calcite, kaolinite, montmorillonite, calcite, aragonite and Palygroskite are identified in rock samples and its wavenumbers are given in Table 1. In all the investigated samples, quartz, calcite and kaolinite are major minerals and others are minor minerals.

5.2.1. Quartz

Crystallinity nature is confirmed from the observed peak at 695 cm\(^{-1}\) for quartz. If the intensity of this peak increases, the crystallinity increases (Mullainathan and Nithiyanantham et al., 2016; Ramasamy et al., 2003). Quartz is the main silicate mineral and identified in all the rock samples. This quartz identified at peak 695 cm\(^{-1}\) due to Si-O symmetrical bending vibrations and 778 cm\(^{-1}\) due to Si-O symmetrical stretching vibrations. In addition to that, quartz found at peak 460 cm\(^{-1}\) Si-O asymmetrical bending vibrations. Some other peaks also found at 1615 cm\(^{-1}\), 1870 cm\(^{-1}\) for quartz due to weathered from metamorphic origin (Ramasamy et al 2009).

5.2.2. Feldspar

Feldspar is one of the most abundant mineral group on Earth. This mineral group includes the orthoclase, microcline and plagioclase feldspars. In the present work, rock samples of AR8, AR9 and AR10 shows the presence of orthoclase feldspar at peak 435 cm\(^{-1}\) due to Si-O asymmetrical bending vibrations and at peak 539 cm\(^{-1}\) due to O-Si (Al)-O symmetrical bending vibrations (Laves, 1960; Ramasamy and Dheenathayalu, 2001; Müller et al. 2014; Papakosta et al., 2020). This band is due to the coupling between the O-Si-O bending vibration and the K-O stretching vibration (Theodosoglou et al., 2010; Matteson and Herron, 1993). Rock samples AR1 and AR2 are convey the presence of orthoclase feldspar at peak 1175 cm\(^{-1}\) due to Si-O stretching vibration whereas other samples show the absence of orthoclase. In addition to that, the presence of microclines is observed by the bands in the region between 1000 and 1100 cm\(^{-1}\). That is, microcline feldspar was recorded at peak 1055 cm\(^{-1}\) due to Si(Al)-O stretching vibrations for the samples AR1, AR2, AR8, AR9 and AR10 and other samples shows absence of this mineral.

5.2.3. Clay minerals

Clay minerals are formed as a result of alteration of such primary minerals as feldspars, micas, chlorides, etc. (Khang, et al., 2016). Clay minerals of montmorillonite and kaolinite are identified in rock samples of Attirampakkam, Tamil Nadu. From the FT-IR spectrum, Si-O-Si and Al-O-Si bands of the mineral lattice around 935, 940 and 535 cm\(^{-1}\) and it clearly show the absorption bands of O-H stretching. There are two narrow and intensive absorption peaks are observed at 3695 and 3625 cm\(^{-1}\) and weak absorption bands are registered at peaks around 3650 and 3665 cm\(^{-1}\) for kaolinite due to O-H stretching. According to Russell (1987), if four peaks are observed in the region 3697–3620 cm\(^{-1}\), the mineral is said to be ordered state. For collected rock samples, the four peaks are observed at 3625, 3650, 3665 and 3695 cm\(^{-1}\) which indicates that mineral is in ordered state. The clay mineral montmorillonite was identified at peaks 479, 1645 and 3440 cm\(^{-1}\) from only samples AR1-AR7. The peak 479 cm\(^{-1}\) appears due to Al-O-Si deformation and peak 1645 cm\(^{-1}\) is due to OH deformation of water. Including with these peaks, strong band 3440cm\(^{-1}\) also observed for montmorillonite due to H-O-H stretching of structural hydroxyl groups and water (Maina et al., 2015). Palygorskite are hydrous Mg silicate clay minerals with fibrous-like morphologies that typically occur as fine-grained, poorly crystalline masses. In the present study, this mineral was identified in the samples AR3-AR7 at peak 515 cm\(^{-1}\) due to Mg (2) octahedral deformation (McKeown et al., 2002).

5.2.4. Carbonate minerals

Carbonate is a key component influencing both chemical and physical properties of samples; it has been accurately estimated by using FTIR spectroscopy (Tinti et al., 2015 Bruckman, et al., 2013; Grinard, et al., 2012). Using obtained FT-IR spectrum, carbonate minerals dolomite and aragonite are identified by peaks at 1445 and 1085 cm\(^{-1}\) respectively. It seems that dolomite peaks appear at shorter wavelengths of spectrum and invariably present in all the samples due to a strong band between 1430 and 1500 cm\(^{-1}\) due to the CO\(_3\)\(^{2-}\) stretching vibration whereas mineral aragonite was found only AR3-AR7.

5.3 Crystallinity index of Quartz:
In the present study, quartz is the major mineral present in all the rock samples, hence the crystallinity index of quartz has been calculated. On the other side, crystallinity of quartz will give a clear indication on the crystalline forms of other minerals because quartz is the mineral, which crystallizes last (Ramasamy and Suresh, 2009). Crystalline samples (natural and synthetic) quartz have the highest values of the index of crystallinity. Minimal variation in crystallinity index shows the sustained processes of crystallization and formation of a committed and well-ordered crystal. A spectrum of x-ray diffraction also reflects the presence of crystallinity (Korovkin et al., 2016). The crystallinity index is calculated using the formula

\[
\text{Crystalline index of quartz} = \frac{I_{778}}{I_{695}}
\]

Where \(I_{778}\) is the intensity of absorption band around 778cm\(^{-1}\) due to the vibrations in tetrahedral site symmetry and \(I_{695}\) is the intensity of the absorption band around 695cm\(^{-1}\) due to the vibrations in octahedral site symmetry. The calculated crystallinity index of quartz is given in Table 3. If the crystallinity index values are greater than 1.00, it is said to be disordered whereas if the crystallinity index values are below 0.75, then it is considered to be ordered crystalline quartz (Ramasamy et al., 2004). The intermediate crystalline quartz is represented by values in between 0.75 to 1.00 (Ramasamy et al., 2004). As seen from table 3, crystallinity index of quartz for all the rock samples are greater than 1.00. This indicates that mineral quartz is disordered in rock samples and variation of crystallinity index of quartz in rock samples are given in Fig 3.

5.4 X-ray diffraction analysis

The recorded XRD spectra of rock samples are shown in Fig 4. The derived peaks and corresponding minerals are given in table 2. Using 2-theta (degree) and d-spacing (Å) of XRD spectrum, various minerals are identified from JCPDS, 2000. The minerals such as quartz, kaolinite, calcite, dolomite, aragonite, hematite and rutile are identified in rock samples. The XRD analysis shows the crystalline and non-crystalline nature of minerals in the samples. That is, above mentioned minerals are confirmed by XRD indicates the crystalline form whereas non-crystalline form was identified for some minerals which are identified through FT-IR only (Suresh et al., 2011).

6. Conclusion

Using FT-IR and XRD techniques, the 10 archeological rock samples of Attirampakkam were analyzed and their mineral composition were identified. The minerals such as quartz, orthoclase feldspar, microcline feldspar, calcite, kaolinite, montmorillonite, calcite, aragonite and Palygroskite are identified in rock samples. From the results, it is inferred that quartz, kaolinite, calcite, dolomite, aragonite in crystalline form and others are non-crystalline form which is also confirmed by XRD technique. However, disordered nature of crystal found in rock samples using crystallinity index of quartz.

References

1. Bruckman VJ, Wriessnig K (2013) Improved soil carbonate determination by FT-IR and X-ray analysis. Environ Chem Lett 11(1):65–70
2. Bunaciu AA, UdriȘTioiu EG, Aboul-Enein HY (2015) X-ray diffraction: instrumentation and applications. Critical reviews in analytical chemistry 45(4):289–299
3. Chauhan PR (2009) The lower Paleolithic of the Indian subcontinent. Evolutionary Anthropology: Issues, News, and Reviews: Issues, News, and Reviews. 18(2):62–78
4. Connolly JR (2007) Elementary crystallography for X-ray diffraction. EPS400-001, Introduction to X-Ray Powder Diffraction, Spring
5. Foote RB (1865) On the Occurrence of Stone Implements in Lateritic Formations in Various Parts in the Madras and. North Arcot Districts
6. Grinand C, Barthes BG, Brunet D, Kouakoua E, Arrouays D, Jolivet C, Caria G, Bernoux M (2012) Prediction of soil organic and inorganic carbon contents at a national scale (France) using mid-infrared reflectance spectroscopy (MIRS). Eur J Soil Sci
7. Ikhane PR, Oyebolu OO, Ehinmowo AA (2020) Mineralogical characterisation of clay deposit near igbile southwestern nigeria. African Journal of Science Nature 6:26–36
8. Karr C (2013) Infrared and Raman spectroscopy of lunar and terrestrial minerals, Oct 22. Elsevier
9. Khang VC, Korovkin MV, Ananyeva LG (2016) September. Identification of clay minerals in reservoir rocks by FTIR spectroscopy. In IOP Conference Series: Earth and Environmental Science, 43,(1), p. 012004
10. Korovkin M, Ananleva L, Nebera T, Antsiferova A (2016) Assessment of quartz materials crystallinity by x-ray diffraction. In IOP Conference Series: Materials Science and Engineering, 110 (1), 012095
11. Laves F (1960) Al / Si distribution, phase transformation and names of alkali feldspars. "Z Kristallogr Kristallgeom" 113:26
12. Maina EW, Wanyika HJ, Gacanja AN (2015) Instrumental Characterization of Montmorillonite Clay by FT-IR and XRD from JKUAT Farm, in the Republic of Kenya. Chemistry Materials Research 7(10):43–49
13. Matteson A, Herron MM (1993) End-member feldspar concentrations determined by FTIR spectral analysis. J Sediment Petrol 63(6):1144–1148
14. McKeown DA, Post JE, Etz ES (2002) Vibrational analysis of palygorskite and sepiolite. Clays Clay Miner 50(5):667–680
15. Mullainathan S, Nithiyanantham S (2013) Elemental Analysis of Some Rock Samples from Namakkal, Tamil Nadu, India. Journal of Advanced Physics 2(4):254–259
16. Mullainathan S, Nithiyanantham S (2016) FTIR spectroscopic studies of rock sediments in Namakkal, Tamil Nadu, South India, for vegetations. Environmental Earth Sciences 75(8):692
17. Müller CM, Pejcic B, Esteban L, Piane CD, Raven M, Mizaikoff B (2014) Infrared attenuated total reflectance spectroscopy: An innovative strategy for analyzing mineral components in energy relevant systems. Sci Rep 4:6764
18. Papakosta V, Lopez-Costas O, Isaksson S (2020) Multi-method (FTIR, XRD, PXRF) analysis of Ertebølle pottery ceramics from Scania, southern Sweden. Archaeometry 62(4):677–693
19. Pappu S, Gunnell Y, Taieb M, Brugal JP, Anupama K, Sukumar R, Kumar A (2003) Excavations at the Paleolithic site of Attirampakkam, south India. Antiquity 77:297
20. Pappu S. Changing trends in the study of a Paleolithic site in India: A century of research at Attirampakkam. In The Evolution and History of Human Populations in South Asia 2007 (pp. 121–135). Springer, Dordrecht
21. Pappu SA (2001) Re-Examination of the Paleolithic Archaeological Record of Northern Tamil Nadu, South India [British Archaological Reports (BAR) International Series 1003. John and Erica Hedges, Oxford
22. Ramasamy V, Dheenathayalu M, Ponnusamy V, Murugesan S, Mullainathan S (2003) Charactersation of quartz and feldspars in white granites. J Curr Sci 3(1):181–190
23. Ramasamy V, Mullainathan S, Murugesan S (2005) Fourier Transform Infrared Analysis of Some Sediments from Palaru River, Tamilnadu, India. Concepts of Biophysics. Pp.125
24. Ramasamy V, Dheenathayalu M (2001) Mineral characterization of feldspar rocks of western ghat. Rajapalayam, Tamilnadu, India. “Bulletin of Pure and Applied Science”, 20F: 15
25. Ramasamy V, Suresh G (2009) Mineral characterization and crystalline nature of quartz in Ponnaiyar River sediments, Tamilnadu, India. American-Eurasian Journal of Scientific Research 4(2):103–107
26. Ramasamy V, Mullainathan S, Murugesan S. Characterisation of minerals and relative distribution of quartz in Cauvery river sediments from Tamilnadu, India – A FTIR Study, Bulletin of Pure and Applied Sciences. 23F (No. 1–2), P. 1–7
27. Ramasamy V, Rajkumar P,Ponnusamy V (2009) Depth wise analysis of recently excavated Vellar river sediments through FTIR and XRD studies. Ind J Phys 83:1295–1308
28. Ravisankar R, Eswaran P, Rajalakshmi A, Chandrasekaran A, Dhinakaran B (2012) Beach rocks from the south east coast of Tamilnadu, India: a spectroscopic study. Advances in Applied Science 3:95
29. Russell JD (1987) “Infrared methods - A Hand Book of determinative methods in clay mineralogy”, Ed. by Wilson, M.J., Blackie and Son Ltd., New York: 133
30. Saravanan D, Veeramuthu K, Rajan K, Kumar VY (2013) FT-IR spectroscopic analysis of archaeological pottery from Arikamedu, Puducherry, India. Physics Research 4:29–31
31. Sciuto C (2018) Carved Mountains and Moving: Stones—Applications of Near Infrared Spectroscopy for Minerals
32. Suresh G, Ramasamy V, Meenakshisundaram V, Venkatachalapathy R, Ponnusamy V (2011) A relationship between the natural radioactivity and mineralogical composition of the Ponnaiyar river sediments, India. J Environ Radioact 102(4):370–377
33. Szczepaniak M. 1 (2014) Rock materials in monuments and archeology – research methods. Geoscience in Archaeometry. Methods and case studies (in this volume)
34. Theodosoglou E, Koroneos A, Soldatos T, Zorba T, Paraskevopoulos KM (2010) Comparative Fourier transform infrared and X-ray powder diffraction analysis of naturally occurred k-feldspars. Bulletin of the Geological Society of Greece 43(5):2752–2761
35. Tinti A, Tognoli V, Bonora S, Francioso O (2015) Recent applications of vibrational mid-Infrared (IR) spectroscopy for studying soil components: a review. Journal of Central European Agriculture 16(1):0–0
36. Wasilewski M (2009) Minerał jako lek – między starożytnością a współczesnością. Minerals as a medicament – between Antiquity and present day. Oficyna Wydawnicza Rytm, Warszawa (in Polish)
37. White JL, Roth CB (1996) Infrared spectrometry. In: Klute A (ed) Methods of soil analysis Part I–Physical and mineralogical methods, 2nd edn. SSSA Book Ser. No. 5, SSSA and ASA, Madison, WI, pp. 291–330

Tables

Table 1 Observed Absorption Frequency in the region of 400 – 4000 cm\(^{-1}\)

| Sample ID | Silicate mineral | Feldspar | Clay Mineral | Carbonate Minerals | Palygrosite |
|-----------|-----------------|----------|--------------|--------------------|-------------|
|           | Quartz          | Orthoclase | Microcline  | Kaolinite         | Montomorilinte | Dolomite | Aragonite |                |
| AR1       | 695, 778, 1615, 1870 | 1175 | 1055 | 535,935, 3625 | 479 | 1441 | - |
| AR2       | 695, 778, 1615, 1870 | 1175 | 1055 | 535,935, 3625 | 479 | 1441 | - |
| AR3       | 458, 695, 779, 1164, 1620 | - | - | 3625, 3665 | 1645 | 1445 | 1085 | 515 |
| AR4       | 458, 695, 779, 1085, 1164, 1620 | - | - | 3625, 3665 | 1645 | 1445 | 1085 | 515 |
| AR5       | 460,695,779, 1875 | - | - | 3625,3650, 3440, 1645 | 1445 | 1085, 1480 | 515 |
| AR6       | 460,695,779, 1875 | - | - | 3625, 3650 | 3440, 1645 | 1445 | 1085, 1480 | 515 |
| AR7       | 460,695,779, 1875 | - | - | 3625,3650, 3440, 1645 | 1445 | 1085, 1480 | 515 |
| AR8       | 695, 778, 1165 | 435,539 | 1055 | 940, 3695 | - | 1440 | - |
| AR9       | 695, 778, 1165 | 435,539 | 1055 | 940, 3695 | - | 1440 | - |
| AR10      | 695, 778, 1165 | 435,539 | 1055 | 940, 3695 | - | 1440 | - |
Table 2  Band assignment of different minerals of archeological rocks

| Minerals                | Frequency | Tentative Assignments                        |
|-------------------------|-----------|----------------------------------------------|
| Quartz                  | 460       | Si-O asymmetrical bending vibration          |
| Quartz                  | 695       | Si-O symmetrical bending vibration           |
| Quartz                  | 778       | Si-O symmetrical stretching vibration        |
| Orthoclase Feldspar     | 435       | Si-O of mixed vibration                      |
| Orthoclase Feldspar     | 539       | Si-O asymmetrical bending vibration          |
| Kaoilinite              | 535       | Si-O asymmetrical bending vibration          |
| Kaoilinite              | 935       | O-H deformation                              |
| Kaoilinite              | 3625      | Inner OH stretching vibrations                |
| Kaoilinite              | 3695      | Inner surface OH stretching vibrations       |
| Montomorilinte          | 3440      | O-H stretching of absorbed water molecule    |

Table 3  Crystallinity index of quartz for the peak 778 cm\(^{-1}\)

| Sample ID | Crystallinity index |
|-----------|---------------------|
| AR1       | 1.1518              |
| AR2       | 1.0900              |
| AR3       | 1.1407              |
| AR4       | 1.0929              |
| AR5       | 1.0535              |
| AR6       | 1.2459              |
| AR7       | 1.1759              |
| AR8       | 1.2140              |
| AR9       | 1.1727              |
| AR10      | 1.2424              |

Table 4 XRD data and its mineral identification of representative sample AR1
| $2 \theta$ (deg.) | d-spacing (Å) | Minerals   |
|------------------|---------------|------------|
| 20.47            | 4.353         | Kaolinite  |
| 26.14            | 3.414         | Quartz     |
| 36.06            | 2.494         | Kaolinite  |
| 39.02            | 2.309         | Calcite    |
| 41.22            | 2.190         | Dolomite   |
| 45.90            | 1.977         | Aragonite  |
| 49.61            | 1.837         | Hematite   |
| 54.36            | 1.689         | Rutile     |
| 60.03            | 1.534         | Quartz     |
| 67.74            | 1.384         | Aragonite  |

**Figures**

The collected rock samples of Archeological site of Attripakkam, Tamil Nadu, India
Figure 2

FT-IR spectrum of rock samples of Archelogical site of Attripakkam, Tamil Nadu, India

Figure 3

Variation of Crystallinity index of Quartz in rock samples
Figure 4

XRD spectrum of rock samples of Archaeological site of Attripakkam, Tamil Nadu, India