Physicochemical and Mineralogical Characterization of the Mediterranean Soils of Triffa Plain (Northeast of Morocco) by the Physicochemical Analysis, X-ray Diffraction and Vis-NIR Spectroscopy

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ABSTRACT

The soils of the Mediterranean regions, characterized by summer aridity and the strong presence of limestone rocks, are dominated by the presence of calcium or even limestone. The soils of the Triffa plain, located in the north-eastern part of Morocco, is a perfect example of the Mediterranean soils. This plain represents one of the most fertile agricultural zones in the north-eastern of Morocco, where all cultivated lands are, dominated by high added values irrigated crops such as Citrus and vegetables. The knowledge of soil characteristics is an important task to better manage these crops. In this context, the main objectives of this study are twofold: 1) to determine the physicochemical proprieties of Triffa plain and their mineralogy using the X-ray diffraction and physicochemical laboratory analysis, and 2). to understand the information provided by the VIS-NIR spectroscopy as it relates to soil mineralogy. To reach these objectives, one hundred eighty-one soil samples were collected from the topsoil horizon (0-30cm) in the study area in 2018. These samples were then analyzed for texture, Organic Matter (OM), Calcium Carbonates (CaCO3), pH, electrical conductivity and potassium. The X-ray diffraction and VIS-NIR spectroscopy were used to determine the soil mineralogy. The results of the physicochemical analysis showed that the soils of the study area are generally belonged to the slightly to moderately calcareous soil classes in term of CaCO3 and are generally basic in term of pH. Concerning the soil organic matter (OM), the study area is characterized by low to medium values of OM content. The soil texture of Triffa plain is dominated by a silt-loam texture. The results of X-ray patterns indicate the dominance of the kaolinite, illite, vermiculite and chlorite, while the mineralogical associations are formed by complex mixtures of carbonates, gypsum, quartz, feldspars and goethite in variable proportions depending on the soil types. Mineralogical diagnostic of VIS-NIR spectroscopy data showed that the absorption bands centered on long waves of 450, 850, 1450, 1950, and 2200 nm are the best bands to be used to study soil mineralogy.

KEYWORDS

X-ray diffraction, Vis-NIR spectroscopy, soil mineralogy, Mediterranean soil, reflectance

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1. Introduction

The soil is a natural resource that fulfils several functions for humans. Its role and functions depend mainly on the nature and quantity of their mineral and organic constituents that influence their physicochemical and mineralogical proprieties. Currently, soils are a necessity, not only to understand their qualities for different uses (agricultural or non-agricultural) but also to ensure their preservation against the factors that threaten their sustainability and against the climate change. Molepo et al. 2017 [1] indicated that soil' physicochemical and mineralogical properties have a strong influence on soil fertility.

The soils of Mediterranean regions, characterized by summer aridity and the strong presence of limestone rocks , do not share a single morphology or common genesis [2]. They are dominated by the presence of calcium or even limestone [3]. In addition, the soils are often clayey and naturally rich in organic matter and calcium, so well-structured and well drained[3].

The determination of clay content by Vis-NIR (Visible and Near Infrared) data measurements is possible in part due to the distinctive spectral signatures of common clay minerals. The Vis-NIR spectrum absorptions by water bonds associated with clay content and other bonding associated with clay type provide the opportunity to use Vis-NIR for quantifying clay information in soil [4]. The clay minerals present in the clay fraction of soils the study of the physicochemical and mineralogical properties of have distinct spectral absorption features, for example the waves with the long waves of 1400 nm and 2200 nm are the spectral absorption of kaolinite [4] and the waves with the long waves of 1400, 1900 and 2200 nm are the characteristic waves of smectite [5].

The soils of the Triffa plain, located in the north-eastern part of Morocco, is a perfect example of the Mediterranean soils. This plain represents one of the most fertile agricultural zones in north-eastern of Morocco, where all land cultivated, are dominated by high added values irrigated crops such as Citrus and vegetable [6]. The determination of soil mineralogy of Triffa plain is a very important step in order to determine the evolution state of soils. The lack of mineralogical studies in this plain is one of the main reasons that led us to carry out this study, which aims to identify and to determine the clay minerals present in the different soil types using the X-ray diffraction and VIS-NIR spectroscopy methods and to characterize their physicochemical properties.

2. Materials and methods

2.1. Study area and soil sampling

The study area is covering a large agricultural land called the Triffa plain located in the north-eastern of Morocco (Fig.1) centered on the geographical coordinates (34°15 N, 2°35' E). It represents the most fertile and productive agricultural area of the eastern Meseta and covers approximately an area of 39400 hectares. The elevation of the study area ranges from 330 to 430 m above sea level and it is characterized by a Mediterranean climate of semiarid type with an average annual precipitation of 676 mm, and a mean annual temperature of 15.8°C [7]. Dahmani et al. [8] indicated that the plain is characterized by an elongated subtriangular shape, bounded to the north by the Mediterranean Sea, to the south by the Beni Snassen mountain range, to the west by Oued Moulouya and to the east by oued Kiss. The Triffa Plain is formed mainly by geological formations of Quaternary, Mesozoic and Cenozoic age, all overlying a Hercynian basement [9]. It is characterized by a diversified pedological cover represented by isohumic, brown calcareous, fersialitic, rendzina, less-developed and hydromorphic soils [10]. The isohumic soils are brown, rich in terms of organic matter and occupy almost half of the study area. Rendzina soils are very dominated in the western part of the plain and correspond to calcimagnesite soils rich in calcium and poor in organic matter, developed from a calcareous parent rock. Hydromorphic soils are characterized by a poorly evolved structure and fine texture, with medium organic matter contents. These soils occupy only small areas of the study area. Fersialitic and brown calcareous soils are rich in organic matter and give the most fertile soils in the zone, while the less-developed soils are poorly acidic soils developed from a non-calcareous parent rock. Soil samples were taken under optimal climatic conditions to have representative samples. The sampling points are chosen in order to cover all the soils studied as shown in **Figure 1**. One hundred eighty-one soil samples were collected from the top soil-horizon (0-30cm) in the study area in 2018. These samples were analyzed for texture, Organic Matter (OM), Calcium Carbonates ($CaCO_3$), pH, electrical conductivity and potassium.

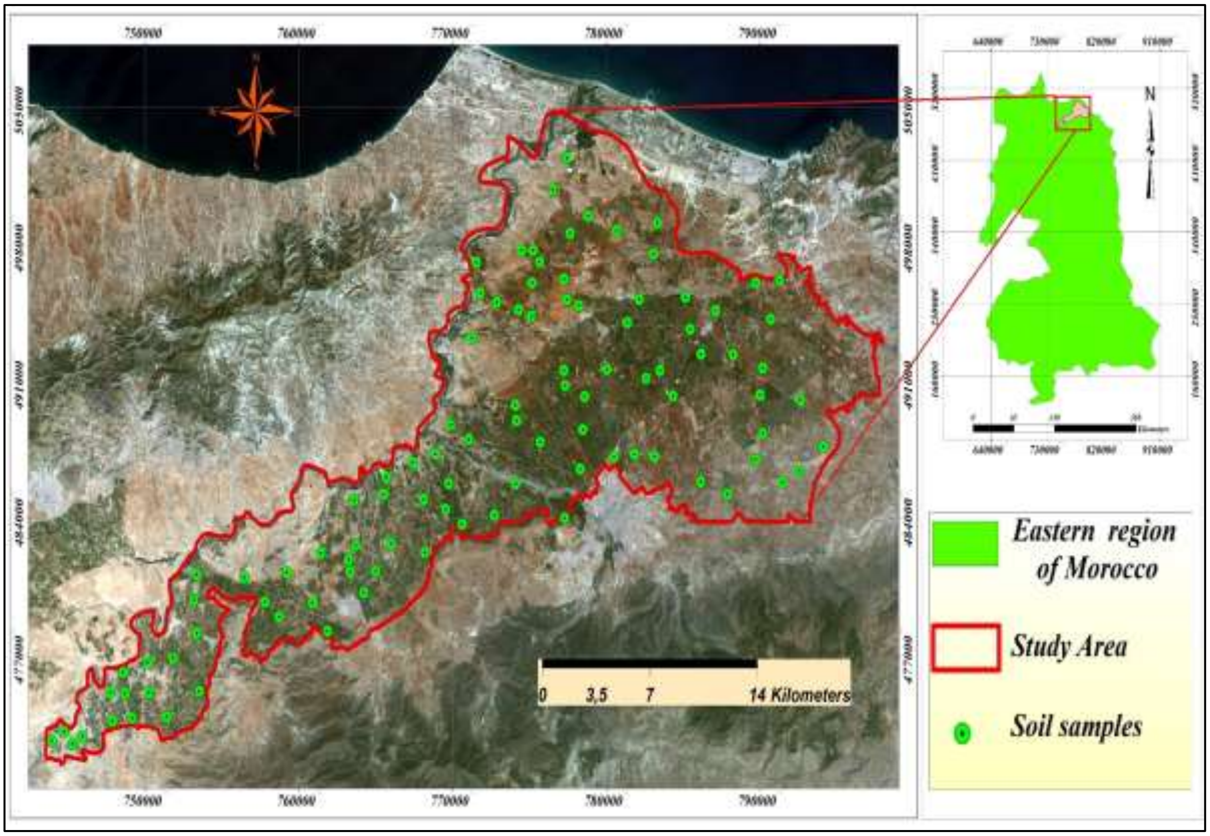

Figure 1: Geographical location of the Triffa Plain.

2.2. Preparation of clay fraction

The extraction and separation of the clay fraction from the soil types of Triffa plain for X-ray analysis requires a well-adopted methodology. The first stage of preparation is the grinding of the samples in an agate mortar for a few, controlling the grinding by passing the sample through a fine sieve. Once the grinding of all the samples is finished, the latter are moved on to another treatment, which is the carbonate test. To ensure suspension of the clay fraction in subsequent treatments, the calcium carbonate samples must be tested. This has been done for all samples with chloridric acid effervescence, using sodium acetates at pH=5 [11]. Once the calcium carbonate samples have been tested, they are further treated to destroy the organic matter using oxygenated water H2O2 (6%) at a temperature of 60°C. Then centrifugation/mixing of the samples is necessary for dispersion of the samples, once the samples are dispersed, the sands are removed by water sieving, then the clays are separated from the silts by a series of sedimentation and siphoning. A centrifugation at 2400 rpm for 40 min allowed to separates the fine clay fraction (< 2 µm) from the coarse fraction (2 to 0.2µm).

2.3. Treatment of oriented blades

The determination of clay minerals is based mainly on the knowledge of the reticular distance or their harmonic [12]. For some minerals, it is difficult to determine their ray from the normal diffractograms (N), such as chlorite, vermiculite and smectite for 14 A° ray. This leads us to make special treatments for the blades in order to judge the nature of clay minerals based on the movement of the ray after the treatments. The first treatment is the solvation with ethylene glycol (EG). The blades are placed for 24 hours in the ethylene glycol atmosphere to ensure the saturation of the clay minerals. This treatment has the effect of swelling the swelling clay minerals causing the displacement of their ray. Another treatment is heating the samples at a temperature of 500°C to destroy certain minerals such as kaolinite and hydrate others such as vermiculite and smectite, which allows to identify and et to discriminate clay minerals.

2.4. X-ray diffraction analyses

A mineralogical characterization of the soils by X-ray diffraction to determine and to identify the clay minerals present in the different soil types of the Triffa Plain was carried out by an X-ray diffractometer of the Bruker D8 ECO type. This analysis was carried out for the three oriented blades of each soil type (normal, ethylene glycol, and heated at 500 °C).

2.5. Spectral measurement

For the spectral measurements, the samples were oven-dried for 24 hours at 45°C, ground and sieved (2 mm mesh) and then placed in Petri dishes (with a diameter of 95 mm and a thickness of 15 mm). Following that, an infra-red intelligent spectroradiometer ASD Fieldspec III Pro (350-2500 nm) was used to measure the Vis–NIR reflectance spectrum of different soil types (Fig.2). The Unscrambler X software was used for preprocessing spectral data.

Figure 2: Schema illustrating the principle of soil reflectance acquisition using the spectroradiometer ASD Fieldspec III Pro.

3. Results and discussion

3.1. Descriptive Statistics of soil datasets

The descriptive statistics of measured soil proprieties are shown in **Table 1**. Soils in the study area are rather alkaline with an average pH of 7.32 and are characterized by sufficient content of plant available phosphorus (P). The calcium carbonates (CaCO3) content indicate that the soils of Triffa plain are slightly to moderately calcareous, our result confirmed those obtained by Lazaar et al. (2019) [10]. The soil salinity (CE) corresponds to the normal values for arable lands. Based on organic matter content, the soils are characterized by OM value varying between 2.39 to 3.34 % which indicates that the different soil types are characterized by medium to high values of organic matter. Soil texture fractions (clay, silt, and sand fractions) for the study area were generally coarse-textured, with low clay content and high silt and sand content, which indicate that soil types of the study area was dominated by a silt-loam texture, this results confirmed those obtained by Lazaar et al. (2019).

Table 1. Descriptive statistics of soil properties of the study area

	Mean	*Max*	*Min*	*Median*	*Variance*	*Std Deviation*
OM (%)	2.39	3.34	0.54	2.48	0.36	0.6
$CaCO_3$(%)	8.28	38.69	0	5.95	58.59	7.65
pH	7.32	7.84	6.82	7.3	0.04	0.19
CE (mS/cm)	0.35	1.33	0.1	0.3	0.04	0.2
P2O5	78.77	357.6	0	56.7	5215	72.22
Clay (%)	5.7	17.5	0	5	14.9	3.86
Silt (%)	52.95	83.5	20.25	54.95	153.7	12.4
Sand (%)	41.35	74.75	16.5	39	160.3	12.66

3.2. Vis-NIR Spectroscopy in Clay Mineral Identification

All clay minerals can be identified using diagnostics bands from 400 nm to 2500 nm of the Vis-NIR spectrum shown in **Figure 3**. The spectra of all soil types present in the Triffa plain have a similar general form with reflectance increasing with increasing of wavelength in the VIS range and present several absorption peaks overlapping near 430, 480, 1400, 1930, 2200, 2260, 2340 nm. The two minor absorption bands discernible in the visible region, one near 430 nm and another near 480 nm are generally attributed to the goethite mineral [13,14]. In the NIR region, According to bishop et al., 2008 [15] the absorbance bands near 1400, 1930, 2200, 2260 and 2340 nm are attributed to the presence of both hydration and crystallization water (vibrational frequencies of OH groups in the water), and the clay minerals. According to [5,15,16] the band near 1400, 1930, 2200 can be associated to the Kaolinite, illite and smectite clay minerals. The bands appear at 2260 nm and 2340 nm are related to Fe-OH and Mg-OH, respectively [17–19]. From this discussion, we conclude that many clay minerals are characterized by same absorption bands for example 1400, 1900 and 2200 nm can be attributed to the kaolinite or smectite or illite. that indicated that the soil spectrum acquired from the Vis-NIR spectroscopy is not sufficient to determine the clay minerals.

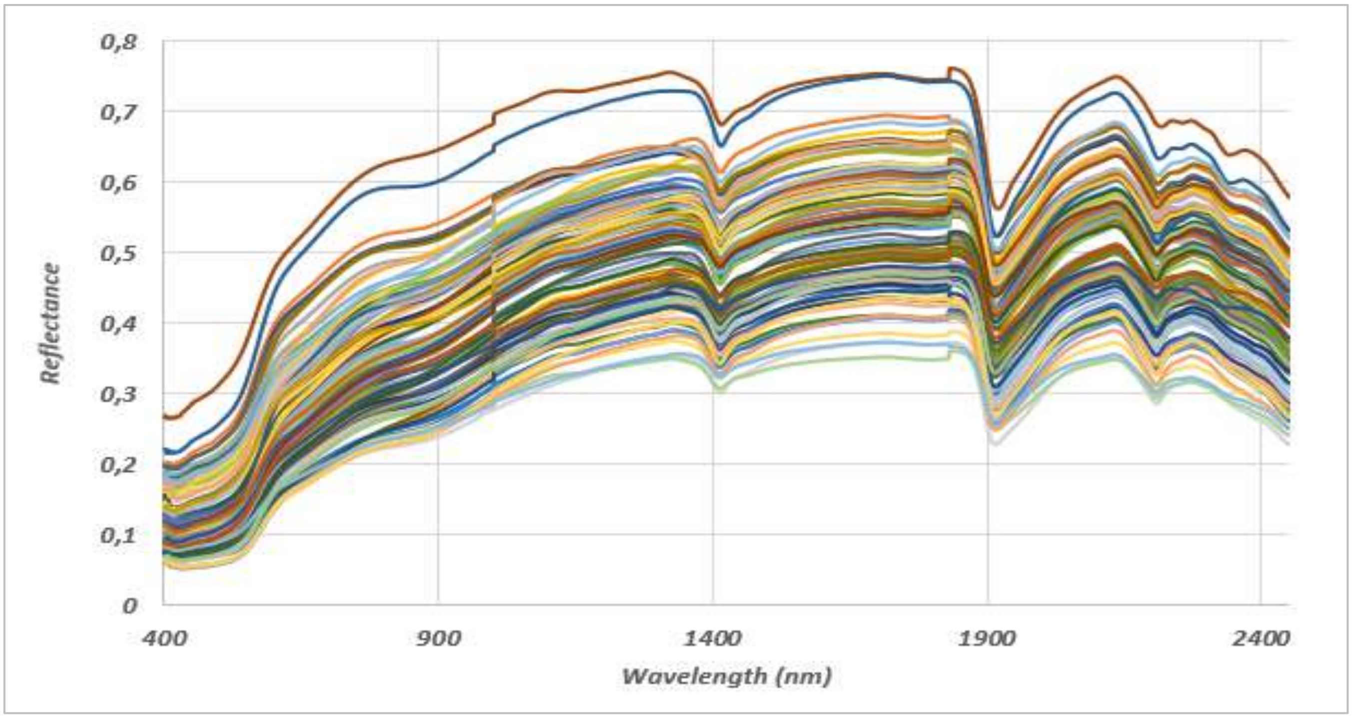

Figure 3: The soil spectra of samples.

3.3. Clay mineral analyses

The mineralogical composition of the studied soils (Rendiza, hydromorphic, less-developed, isohumic, fersialitic and brown calcareous soils) is summarized in **Figure 4**. The XRD pattern of the oriented blades of all soil types studied show that the kaolinite, illite, vermiculite and chlorite are the major clay minerals identified in all soil types of the Triffa plain. For the isohumic, less-developed, rendzina, Fersialitic and brown calcareous topsoils, the illite, kaolinite and vermiculite are the dominants clay minerals associated with chlorite. Concerning the hydromorphic soil is characterized by the presence of the kaolinite, illite and vermiculite and the absence of the chlorite. Our results confirm partially those obtained by packet (1970) [20] which has found that in the shallow soil horizons, attapulgite is still absent and the clay fraction consists mainly of illite and chlorite. In addition to these minerals cited by Paquet (1970) [20]our study also found the presence of kaolinite and vermiculite.

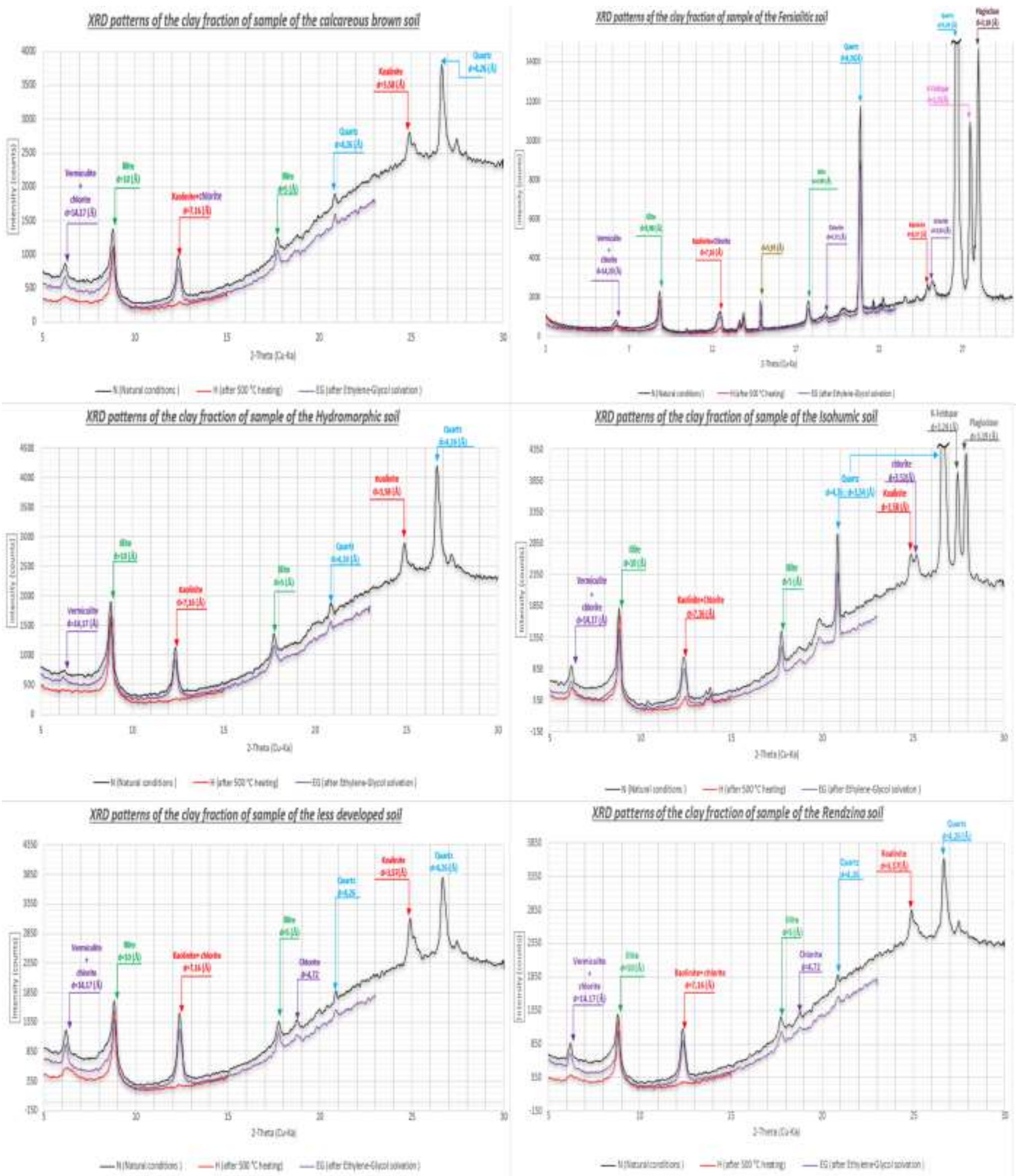

Figure 4: XRD diffractogram of the clay fraction of the different topsoil types of Triffa plain.

3.4. Bulk minerals analyses of soils

The bulk mineral analyses of the different topsoils of Triffa plain are illustrated in **Figure 5**. The principal mineralogical associations of the samples are formed by complex mixtures:
Isohumic soils: total clay, calcite, quartz, plagioclase, and goethite.

- Less-developed soils: total clay, calcite, pyrite, quartz, plagioclase, aragonite and goethite.
- Fersialitic soils: total clay, calcite, siderite, quartz, K-feldspars, plagioclase, aragonite, pyrite and goethite.
- Rendzina soils: total clay, calcite, quartz, K-feldspars, plagioclase, aragonite and goethite.
- Hydromorphic soils : illite, quartz, calcite, plagioclase, aragonite and goethite.
- Brown calcareous soils: total clay, calcite, quartz, plagioclase, aragonite, and goethite.

This result conduct to conclude that all soil samples present same mineralogical association with minor differences in the hydromorphic and fersialitic soils present the siderite and illite respectively.

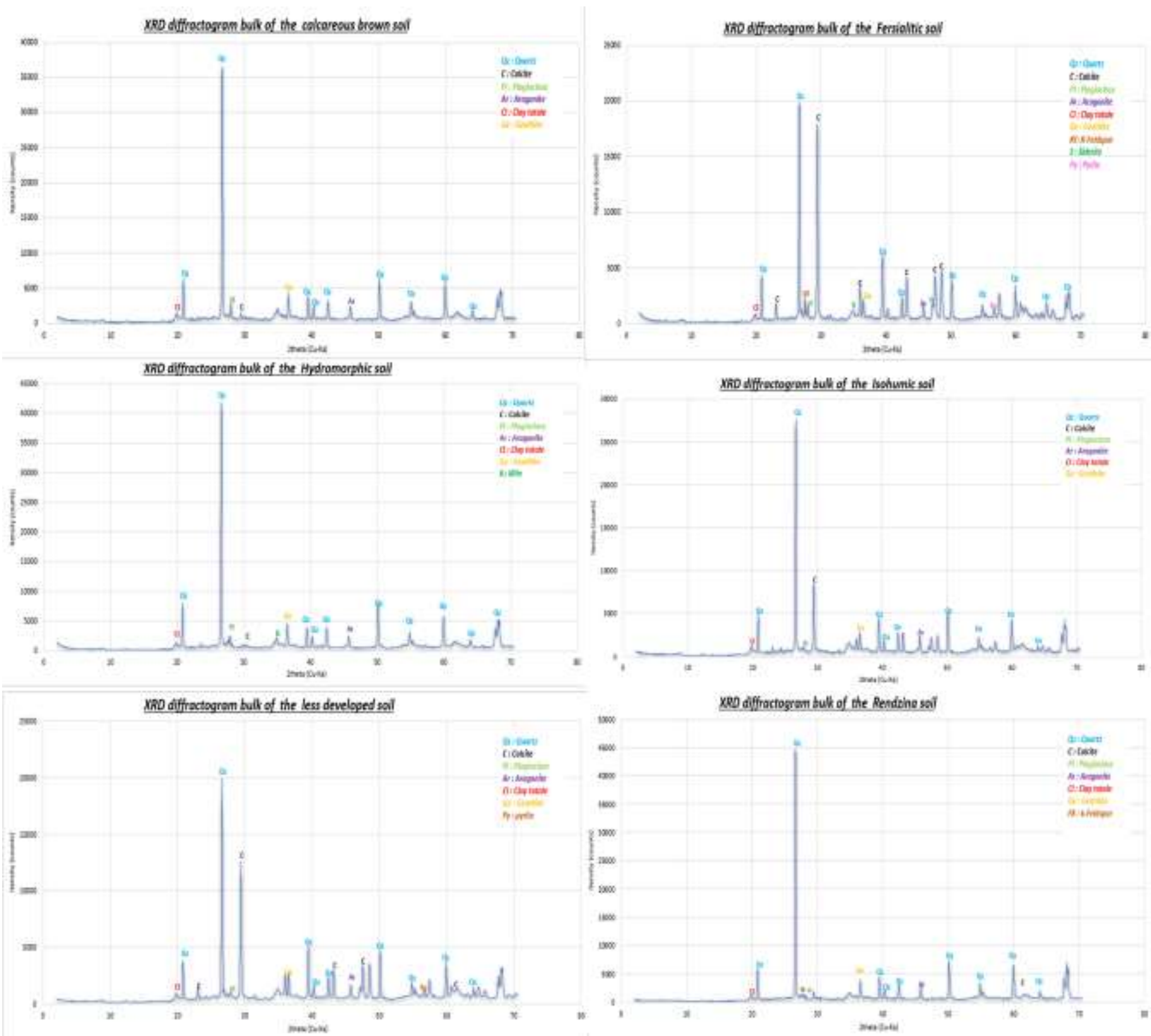

Figure 5: XRD diffractogram bulk of different soil types of Triffa plain.

4. Conclusion

Sampling, analysis and examination of the soil of Triffa plain in order to assess its status and their physicochemical and mineralogical characterizations allows to conclude that the Triffa plain are characterized by soils of good quality and the potential of Vis-Nir spectroscopy is not sufficient to determine the clays minerals present in different soil types. The major dominant clay minerals in different topsoil are the Kaolinite, illite, chlorite and vermiculite, while the mineralogical associations are formed by complex mixtures of calcite, siderite, attapulgite, quartz, K-feldspars, Plagioclase and goethite in variable proportions.

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