

Characterization of A Hard Opaline Clayey Bed Overlying Phosphates from Esh-Shidiya Area, SE of Jordan.

Zayed Al-Hawari *

Department of Environmental and Applied Geology, University of Jordan, Amman 11942, Jordan.

Abstract

The top two meters of a yellowish clayey bed in Esh-Shidiya area are characterized by using X-ray diffraction (XRD), X-ray fluorescence (XRF), and Scanning electron microscope techniques. The clay rich bed is composed of dioctahedral smectite (100% expandability), quartz, and goethite. The SEM photos have indicated that there is a close relationship between the dioctahedral smectite and silica phases (quartz and amorphous silica). The porous nature of the silica rich bed that overlies a porcelanite (tripoli) layer and the nature of the continuous growth of smectite plates suggest a diatomite rich precursor.

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1. Introduction

Clays of different origin are widely distributed in Jordan. Economical clays are found in different stratigraphic units from Paleozoic to Cenozoic time. Kaolinite, bentonite, and palygorskite deposits are among the most important commodities. Some clay beds are associated with Jordanian phosphorites.

Phosphorites are currently mined from Esh-Shidiya area. The future phosphorite industry in the Esh-Shidiya area is estimated around more than 1000 million tons of reserve. The area is located to the south-east of Jordan, approximately 50km south-east of Ma'an (Figure1). The geology and mineralogy of the clays in this area were reported by Khaled (1980). He mentioned that montmorillonite, kaolinite, and mixed-layer illite/smectite are the essential clay minerals that are associated with Esh-Shidiya phosphates. Other studies have concentrated on the phosphorite petrology, geochemistry, and phosphogenesis (Abed et al. 2005), Abed and Abu Murry (1997) studied the rare earth elements distribution, and concluded that upwelling currents played an important role in the deposition of Esh-Shidiya phosphorites. Zghoul(1997) studied the genesis of the palygorskite in the upper part of the sequence overlying phosphorite deposits, and concluded that it was formed from a hypersaline restricted platform or lagoons. Abed et al.(2007) studied evolution of Esh- Shidiya phosphorites, and concluded that palygorskite is of authigenic origin. Systematic study on some clays was carried out by Khoury et. al.(1988). They reported, for the first time, the presence of palygorskite associated with mixed-layer illite/smectite and kaolinite in the phosphatic beds and marls. The top yellow flat opaline like clayey bed was never investigated. The aim of this

paper is to characterize the opaline clayey bed towards the top of the phosphorite sequence in Esh- Shidiya area.

2. Geological Setting

Esh-Shidiya phosphorites are situated in the extreme SE Jordan. It is Upper Cretaceous in age, lower Maastrichtian (Khaled & Abed 1982).High grade phosphorites reserves in this area are around 1000 million tons. Esh-Shidiya phosphorites consist of four phosphorite beds designated from bottom to top: A3, A2, A1, and A0. They are separated by non phosphate materials like chert, marl, dolomitic clay, and porcelanite. These deposits are overlain by yellow marl with varying thickness. The marl is overlain by thick red soil and reddish fluvial conglomerate.

The horizon under investigation is a hard opaline silica horizon. It is tow meters thick, yellow in colour; and is present towards the top of Esh- Shidiya section. It is overlain by the reddish soil and conglomerates and underlain by 0.3m chert, which makes the topmost part of Esh-Shidiya phosphorites (Fig 2).

3. Methodology:

A representative sample was collected from the yellow clayey opaline bed. X-ray diffraction (XRD), X-ray fluorescence (XRF), and Scanning electron microscope studies were carried out to characterize the clay sample. The samples were characterized using mineralogical and chemical methods. Size fractionation and the separation of the clay, silt and sand size fractions were accomplished using Atterberg techniques (Jackson, 1975). The cation exchange capacity of the clay was measured using calcium saturation method (Jackson, 1975).

All the analytical work (XRD, XRF, IR and SEM) was carried out in the laboratories of the Federal Institute for Geosciences and Natural Resources, Hanover, Germany.

* Corresponding author.hawariza@yahoo.com;

A Philips diffractometer PW 3710 (40 kV, 30 mA) with CuK_α radiation, equipped with a fixed divergence slit and a secondary graphite monochromator were used. Whole rock 'random powder' samples were scanned with a step size of $0.02^\circ 2\theta$ and counting time of 0.5 s per step over a measuring range of 2 to $65^\circ 2\theta$.

Powdered samples were analyzed using a PAN analytical Axios and a PW2400 spectrometer. Samples were prepared by mixing them with a flux material and melting into glass beads. The beads were analyzed by wavelength dispersive x-ray fluorescence spectrometry (WD-XRF). To determine loss on ignition (LOI), 1000 mg of sample material were heated to 1030°C for 10 min. After mixing the residue with 5.0 g lithium metaborate and 25 mg lithium bromide, it was fused at 1200°C for 20 min. The calibrations were validated by analysis of Reference Materials. "Monitor" samples and 130 certified reference materials (CRM) were used for the correction procedures.

An ESEM- FEI Quanta 600 FEG scanning electron microscope, operated in low-vacuum mode (0.6 mbar), was used for optical characterization on the μm scale. Therefore, sputtering of the samples with gold or carbon was not necessary. An EDX-system Genesis 4000 of EDAX was used for chemical characterization.

The infrared samples were prepared using KBr discs; and were studied by using Nexus FT- IR Thermo Nicolet 150°C dry.

4. Results:

The opaline-like soft clay bed is yellowish to brownish in color due to iron oxides-hydroxides. The hand specimens look dense, but are light in weight. The sampled bed is overlain by porous iron-rich alluvial deposits and underlain by porcelanite (tripoli) layer (Fig. 2).

Fig. 3 shows a typical X-ray diffractogram of the random whole rock preparation of the clayey bed. The diffractogram indicates that the sample is composed of smectite, quartz, and goethite. The same composition is also indicated in the silt size fraction (Fig. 4). The oriented X-ray runs of the clay size fraction have indicated the presence of smectite with 100% expandability and quartz as the essential constituents (Fig. 5). Traces of opal-CT are also indicated by the presence of 4.18 \AA reflection. The basal reflections of the oriented aggregates are indicated in (Fig. 5). The basal (001) reflection of the dry oriented preparation appears at 12.6 \AA . The 12.6 \AA basal reflection expands to 16.9 \AA upon glycolation.

The chemical composition of the clay and silt size fractions of sample KH16 is given in Table 1. SiO_2 content is related to quartz, opal-CT and smectites. Al_2O_3 , MgO , CaO , K_2O , and Na_2O content are related to the crystal chemistry of smectite. Fe_2O_3 and TiO_2 are possibly related to both smectite and goethite. P_2O_5 is related to some traces of apatite. Loss on ignition (LOI) is related to adsorbed and structural water in the smectite and goethite. The trace elements As, Cr, Cu, Ga, Rb, and V are enriched in the clay size fraction; and possibly enriched in the smectite. Ba, Co, Mo, Ni, Pb, Sr, Zn and Zr are higher in the silt size fraction

The most unique property of smectite minerals is the presence of exchangeable cations that are primarily

adsorbed on the sheet surfaces. The cation exchange capacity of the clay fraction is 30 meq/100g. The most possible exchangeable ions are Ca, Na, and K as indicated from the EDX and chemical results.

The scanning electron micrographs indicate that some phosphate materials (bones) are embedded in the fine matrix (Fig. 6). The texture is homogeneous porous with a dominating crystal size less than 2 microns (Fig. 6). The SEM photos indicate that smectite crystals range in size between 2 microns and 0.2 microns with an average size of about 0.5microns. The matrix is made up of smectite and silica phases, mostly quartz and opal-CT. Fig. 7 shows the continuous growth nature of smectite plates in addition to radial oriented growth. Smectites are found in aggregates, and the neofomed crystals are bridging between the silica phases and grow freely at the expense of the silica phases. The continuous growth of the smectite sheets is well illustrated in (Fig. 8). The lath shaped morphology of the crystallites is dominant, but hexagonal and fibrous varieties are also present.

The EDX results as indicated in (Fig. 9) illustrate that Al and Si are the essential constituents of smectite. Mg and Fe are also present in the smectite structure possibly substituting for Al in the octahedral layer. Fig. 9 indicates also that Ca, K and Na are present in minor amounts possibly as interlayer cations.

The smectite type is a dioctahedral low magnesium type as indicated in (Fig.10). The infrared spectrum confirms the X-ray and SEM results by showing a dioctahedral layer silicate (smectite) and silica phases. The OH water absorbs at 3400 cm^{-1} . The absorption pattern for the stretching vibrations of the structural OH groups (the principal band at 3560 cm^{-1}).

5. Discussion:

The studied clay rich bed is composed of dioctahedral smectite (100% expandability) with quartz and goethite. The field work has indicated that there is a close relation between the dioctahedral smectite and silica phases (quartz and amorphous silica). The porous nature of the silica rich bed that overlies a porcelanite (tripoli) layer suggests a diatomite rich precursor. The released silica from the dissolved frustules is mostly consumed during the growth and neoformation of smectites, opal-CT, and microcrystalline quartz. The transformation of opal-A to opal-CT and finally to quartz is illustrated by Khoury, (1989) and Hesse, (1988). Smectites with a continuous non-interrupted continuous crystal growth indicates a neoformation process possibly as direct crystallization from solution. The radial continuous oriented growth indicates a transformation process from silica phases possibly quartz. The SEM study suggests that the dissolution of diatomite frustules has led to the formation of opal-CT and quartz (Khoury, and Qadan, 2003). The presence of a silica source has helped in the neoformation of smectite. The circulating water moving from the overlying red conglomerate has carried dissolved cations that are incorporated in the structure of smectite. So, the age of smectite is most probably of Pleistocene to Recent.

The most unique property of smectite minerals is the presence of exchangeable cations that are primarily adsorbed on the sheet surfaces.

Table 1: Major oxides and trace elements composition of the clay sample (KH16).

Sample No	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Sum
	%	%	%	%	%	%	%	%	%	%	%	%
KH16/12 Clay Size	68.12	0.406	9.45	7.14	0.054	1.41	0.634	2.36	0.437	0.483	9.16	99.76
KH16/13 Silt Size	75.58	0.46	6.36	6.37	0.225	1.01	1.184	0.03	0.305	0.29	7.87	99.67

Sample No.	(As)	Ba	Ce	Co	Cr	Cu	Ga	Mo	Nb	Nd	Ni	Pb	Rb	Sb	Sc	Sm	Sn	Sr	U	V	Y	Zn	Zr
KH16/12 Clay Size	24	135	<20	9	226	45	11	7	6	<50	65	39	19	6	8	<50	<2	22	3	299	3	276	50
KH16/13 Silt Size	19	601	21	18	127	32	8	13	6	<50	68	42	15	<5	6	<50	10	77	4	275	6	325	67

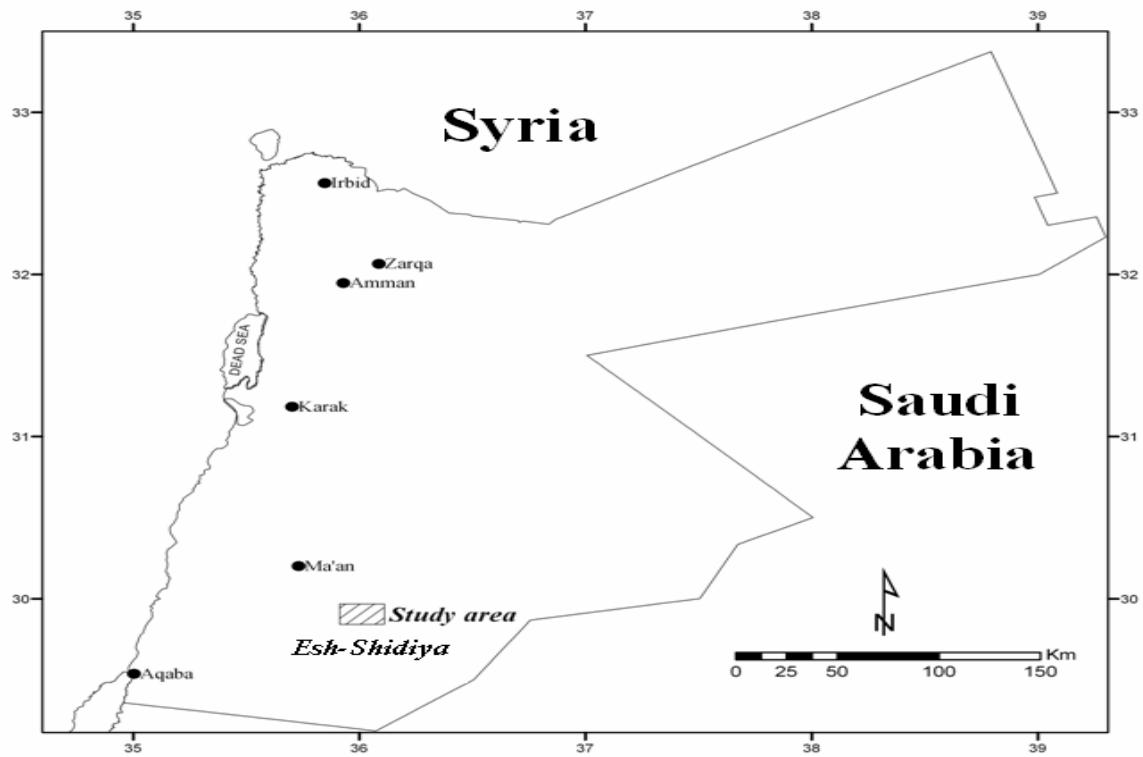


Figure 1. Location map of Esh-Shidiya area

Sample No.	Thickness (m)	Lithology	description
KH16	3 m	[Symbol]	Reddish alluvial sediments
	2 m	[Symbol]	Yellowish hard clay (opaline clay) (Location of the composite sample)
	0.3 m	[Symbol]	Chert and tripoli
	0.2 m	[Symbol]	Clay
	2.5 m	[Symbol]	Thin layers of cherty phosphate and clayey phosphate
	1.5 m	[Symbol]	Soft phosphate (A0)

Figure 2: Columnar section of the upper part of Esh-Shidiya area.

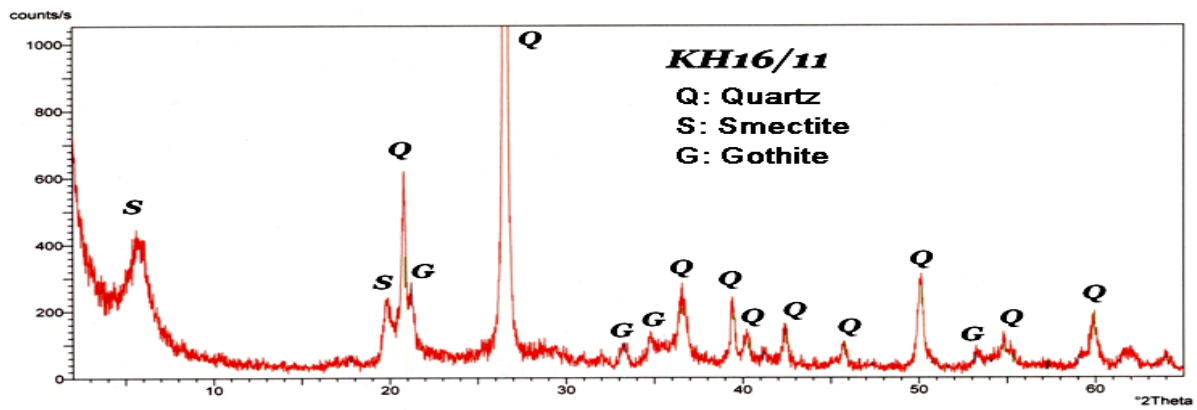


Figure 3 : A trace of X-Ray Diffractogram of the wholeRock Sample (KH16). Figure 4: A trace of X-Ray Diffractogram of the silt size fraction(sample KH16).

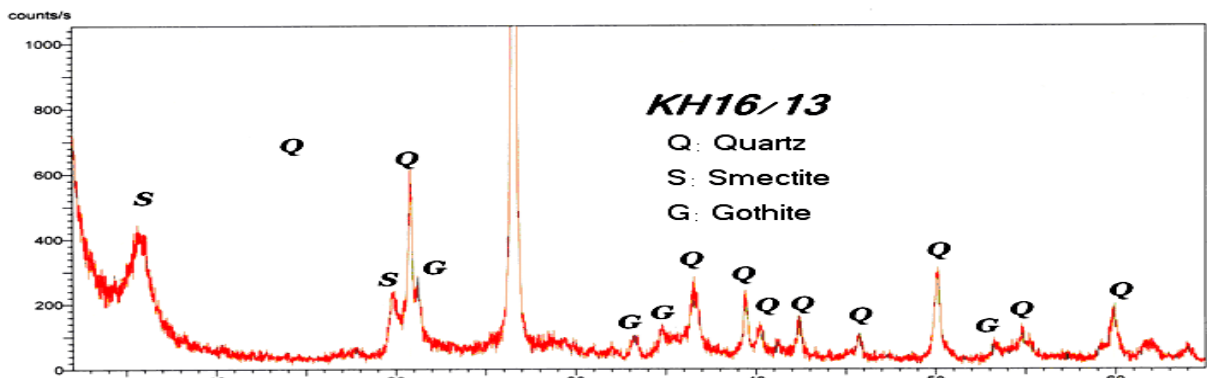


Figure 4: A trace of X-Ray Diffractogram of the silt size fraction (sample KH16).

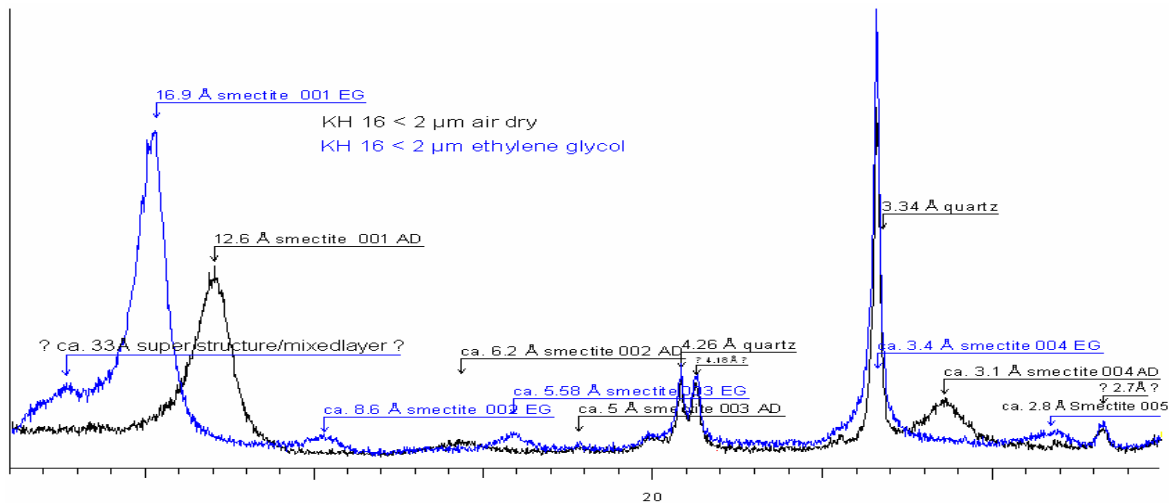


Figure 5: A trace of X-Ray Diffractogram of the clay size fraction sample (KH16).

The aggregation character can have an important influence on physical and rheological properties. This property is very important for using the smectites of the clayey bed for drilling mud.

6. Conclusions:

The SEM investigations have indicated that the silica rich bed is formed as a result of diagenetic transformation

process. A diatomite rich precursor (opal-A) is, most probably, the source for silica that has formed dioctahedral smectitic clay and quartz. The clay bed could be utilized for industrial applications.

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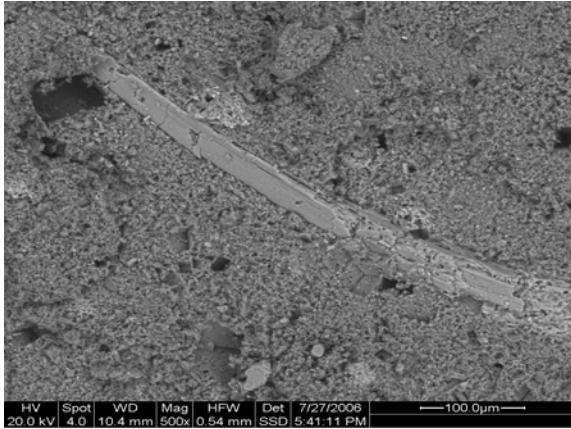


Figure 6: SEM photomicrograph of apatite bone embedded in a clayey matrix.

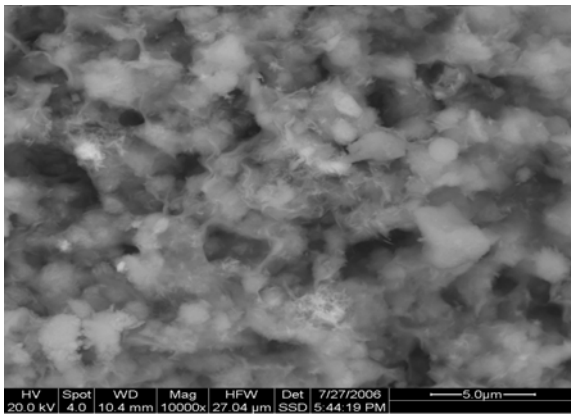


Figure 7: SEM photomicrograph of intergrown smectites with quartz and opaline phases, High porosity.

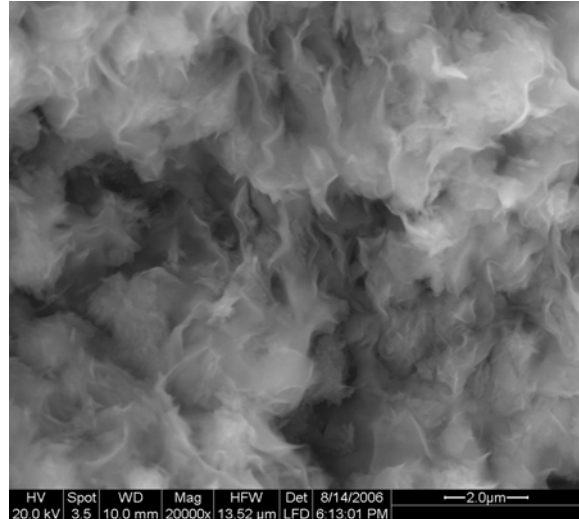


Figure 8: SEM photomicrograph of smectite (Sample KH16) showing a continuous intergrowth.

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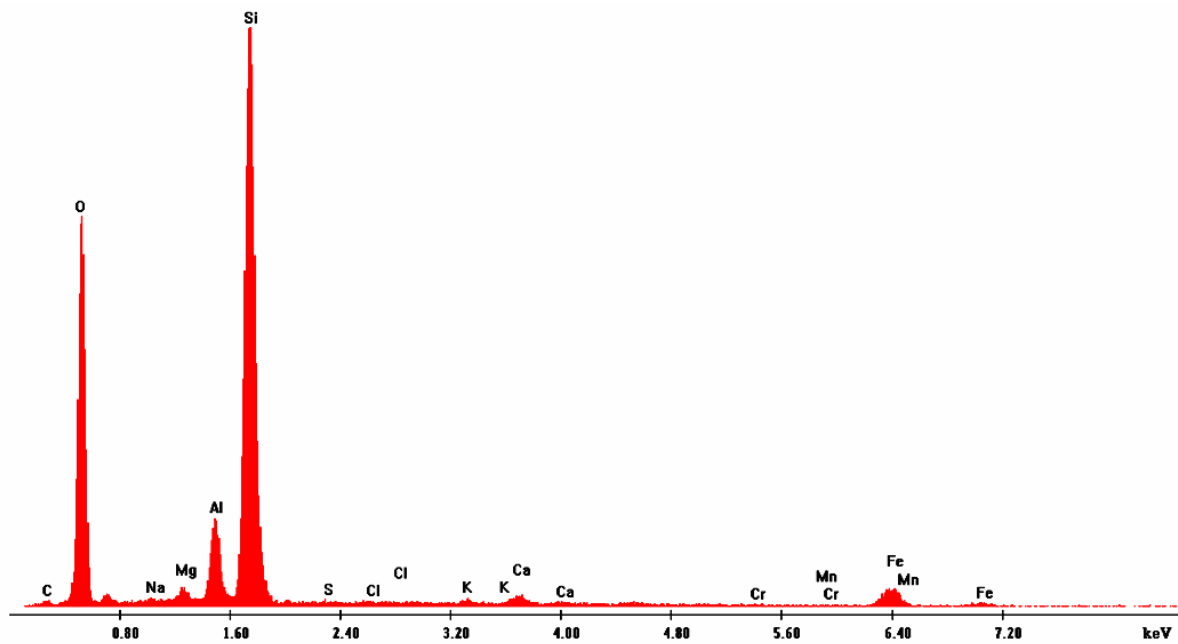


Figure 9:EDX Results of the Smectite of Sample (KH16).

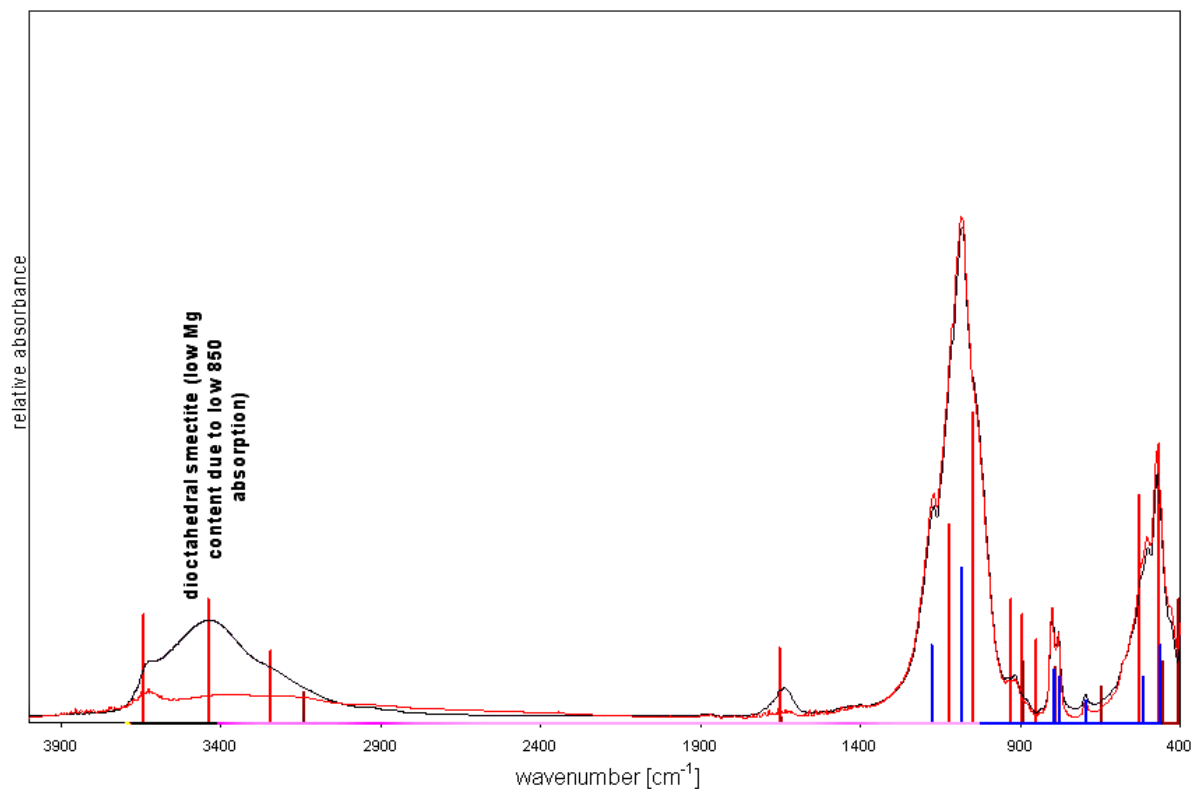


Figure 10: Infrared absorption spectra of the clay size fraction of sample (KH16)

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