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Full Length Research Paper

Evaluation of thermal mud characteristics of Erzurum (Köprüköy) clayey raw materials (NE Turkey)

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In Turkey, there are several natural occurrences of clays/muds which are used for therapeutic, aesthetic, and pharmaceutical purposes. The aim of this study was to assess the mineralogical and physicochemical properties of Erzurum clayey raw materials from Koprukoy (Erzurum, NE Turkey) for their therapeutic purposes. Raw material samples were collected from Pliocene geological formation deposited in the lacustrine environment and located Koprukoy (Erzurum) thermal area. The samples of geological formation including some fossil were tested by X-ray powder refraction and diffraction methods to determine the mineralogical and physicochemical properties. The experimental results showed that smectite clay mineral was abundant, as well as kaolinite, illite, zeolite, mica, quartz, calcite, plagioclase, feldspar and non-clay minerals. Physicochemical properties, such as specific surface area, cation exchange capacity and plasticity index were also determined using ammonium acetate, ethylene glycol mono ethylene ether and consistency test methods, respectively. From the physicochemical' chemical and mineralogical properties, all samples have thermal properties, which make them potentially suitable for therapeutic or aesthetic purposes.

Key words: Clayey material, thermal mud, clay mineralogy, technological property, pelotherapy.

INTRODUCTİON

Peloids are muds, or clayey soil materials used therapeutically, as part of balneotherapy, or therapeutic bathing. They consist of humus and minerals formed over many years by geological, biological, chemical and physical processes. The term "peloid" is used to refer to different kinds of sediments or deposits whose compositions include mainly silicates (micas, clays, feldispars) carbonates sulphates, sulphides and variable amounts of organic substances. Peloids have been used as thermal therapeutic agents in many spas and thermal centers since ancient times (Legido et al., 2007).

There is a long tradition in using peloids for cosmetic and medical purposes. It is well known from historical sources that in Ancient Egypt, Greece and Rome muds were used as antiseptic cataplasms to cure skin, stomach and intestinal ailments, as well as for cosmetic purposes.

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In modern medicine, the use of healing muds in pharmaceutical formulations, in spas and in aesthetic medicine increased during the few years due to the increasing interest in and success of natural remedies (Mascolo et al., 1999; Carretero, 2002; Veniale et al., 2004; Vreca and Dolennec, 2005).

In recent times, researches on the thermophysical properties and the therapeutic effects of peloids have been carried out, particularly in the fields of rheumatology and dermatology (Bellometti et al., 2000; Cara et al., 2000; Beer et al., 2003; Argenziano et al., 2004; Codish et al., 2005; Rebelo et al., 2010). In pharmaceutical formulations, they are used as gastrointestinal protectors, oral laxatives, anti-diarrheals, dermatological protectors and cosmetics. The main factors determining the nature of a peloid are the composition and granulometry of the initial clay, its cooling rate, the composition of the mineral water used for the mixture and the type of maturation process (Curini et al., 1990; Sanchez et al., 2002). For a clay paste or peloid to be suitable for pelotherapy, it should have several properties, such as low cooling rate, high absorption capacity, high cation exchange capacity, good adhesiveness, ease of handling and a pleasant feeling when applied to the skin (Carretero et al., 2006; Veniale et al., 2006). The mineralogical composition and granulometry of the initial form of the clay and the composition of the mineral water used for the mixture are also important (Curini et al., 1990; Carretero et al., 2007; Gomes and Silva, 2007; Tateo and Summa 2007; Veniale et al., 2007; Tateo et al., 2009). Textural differences between structurally and chemically identical minerals also affect their adsorptive and rheological properties (Lagaly, 1989; Murray and Keller, 1993; Karakaya et al., 2010).

Clayey raw materials of the Koprukoy (Erzurum) thermal mud area is expansive and over-consolidated fissured clayey and marl soils. These geological units are found in abundance in Northern and Western part of Koprukoy city and its many villages such as Badicivan. Modern alluvial deposits generally cover these units. The objective of this study was to determine the properties of Koprukoy (Erzurum) clayey raw materials, which are used as thermal muds.

GEOLOGY

Koprukoy (Erzurum) clayey raw materials lie at approximately 50 km East of Erzurum between Latitudes 39°56′ to 40°07′ N and Longitudes 41°46′ to 41°56′ E, Turkey. This area is located on the Erzurum-Kars Plateau (near the Southern margin), which was formed by extensive Miocene-Quaternary thick lave-pyroclastic flows with clastic sedimentary intercalations. In this region, early studies were conducted on the oil exploration between Pasinler (Erzurum) and Horasan (Rather, 1969), on the surface fractures of 1984 Horasan (Erzurum) earthquake (Kocyigit, 1985) and on the geology of Koprukoy thermal mud area and geothermal energy possibility (Dagistan, 2001). Also, the volcano-stratigraphy of Erzurum-Kars Volcanic Plateau (Keskin, 1998) and the history of collisional tectonism in the eastern Anatolia (Sengor and Kidd, 1979; Sengor and Yilmaz, 1981; Barka et al., 1987; Bayraktutan, 1999) were studied.

The study area consists of Miocene, Pliocene and Quaternary units (Figure 1). These units are almost unconformity among each other, with some exceptions of conformable at several locations. The Upper Miocene units, the oldest units of region are represented by basalt and pyroclastic, black andesite and black ignimbrite formations. The basalts and pyroclastic consist of black basalt, ignimbrite and agglomerate. The black andesite (hornblende), tuffite and tuff with obsidian compose of black andesite. The black ignimbrites are represented by black and red ignimbrites including volcanic bomb. The Pliocene units take place as unconformity on the Upper Miocene units. These units begin volcanic rocks composed of rhyolitic, andesitic and trachytic lava including pink and white ignimbrites. Horasan formation comes on the volcanic rocks with unconformity. This formation deposited in the lacustrine environment consists of fine grained conglomerate, sandstone and marl. Horasan formation includes tuffite and clay intermediate levels in some places. Sandstone with fine granular and shale-marl with yellow color get involved in the upper side of this formation. These levels consist of some fossils such as *Dreissensia* sp., *Gastropoda* sp. *and Congeria* sp. (Rather, 1969). Quaternary units forming from old and young alluvium deposits consist of gravel, sand, silt and clay particles. These particles represent particles of all old units in the region (Yilmaz et al., 1988; Keskin, 1998; Dagistan, 2001) (Figure 1).

Koprukoy (Erzurum) thermal mud area lies on the Erzurum Fault Zone. The existence of an approximately ENE-WSW trending zone of sinistral transpression is expressed and in by vertical sinistral transcurrent faults, marginal belts of oppositely vergent thrust faults and E-W trending folds and N-S trending tensional fractures, which were conduits for pre-Pliocene calc-alkaline volcanic. This structure, identified as Erzurum Fault Zone, dates from Late Miocene and is represented by a 400 km long and 10 to 25 km wide sinistral active fault zone. The Erzurum Fault Zone is composed of ENE-WSW trending sub-parallel right-stepping strike-slip fault segments with varying amounts of reverse displacements on them. There are also volcanic extrusions in zones of tensional stress along the Erzurum Fault Zone, and in the region of eastern Anatolia-Lesser Caucasia in general (Bayraktutan et al., 1996; Bayraktutan, 1999).

The Koprukoy (Erzurum) thermal mud area occurs in the intersection point of right-stepping and left-stepping strike-slip fault segments. The right-stepping strike-slip fault segment extends NNE-SSW trending and the left-stepping strike-slip fault segment extends ENE-WSW trending (Figure 1). The Koprukoy (Erzurum) thermal mud area is located on the Horasan formation forming under control of these segments of the Erzurum Fault Zone, which is one of the most active fault belts of the East Anatolian Region. Historical records of destructive earthquakes, morphtectonic features formed by paleo-seismic events and instrument seismic data of region indicate to a very high regional seismicity (Bayraktutan et al., 1996).

MATERIALS AND METHODS

Sampling and description of the studied materials

The clayey raw materials used in this study were collected from Horasan Formation in the Koprukoy (Erzurum) thermal mud area (Figure 1). To achieve representation of lateral change in facies, samplings were performed at the three different locations of Pliocene sedimentary sequence. These locations were selected as starting point of the thermal water, its 100 m North side and its 100 m South side. The sampling was carried out at different levels representing different units at the vertical direction. In the starting point of the thermal water, disturbed soil samples were

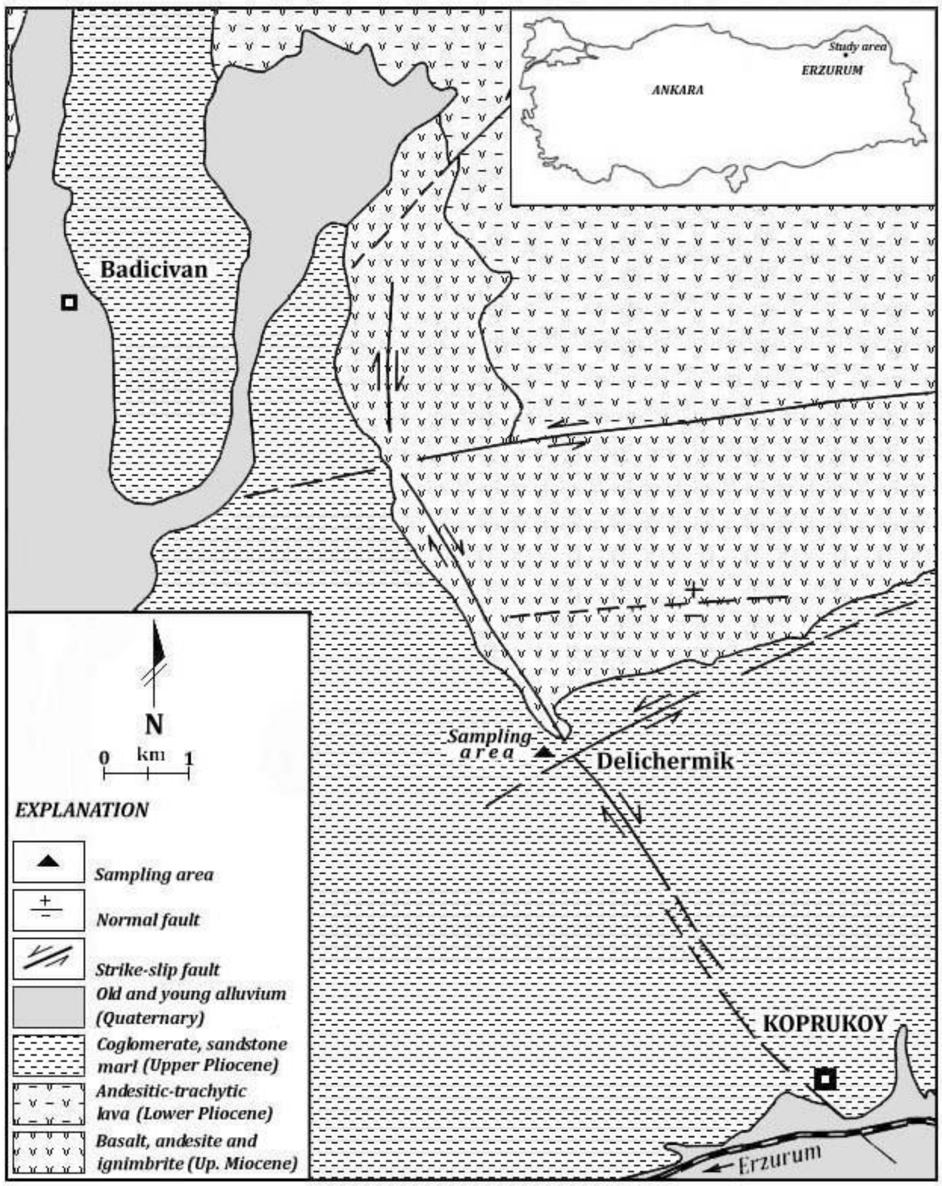


Figure 1. Geological map of Koprukoy (Erzurum) thermal mud area.

collected from the splitting of geological unit at 7.5 m. In the Southern and Northern of starting point, disturbed soil samples were collected from the investigation pits at 1.8 and 2.4 m, respectively. In this study, the samples of Koprukoy (Erzurum) thermal mud were labeled as central samples of Koprukoy thermal mud (KCS), Northern samples of Koprukoy thermal mud (KNS) and Southern samples of Koprukoy thermal mud (KSS).

Laboratory analysis

Sieve and hydrometer analyses were carried out to determine grain size distribution of clayey materials. Grain size distributions tests were performed in two stage processes. First, the samples were wet sieved to separate the coarser particles (>74-μm) in accordance with ASTM D 421 and then subjected to decantation to obtain the finer fraction (<74-μm) in accordance with ASTM D 422. The liquid limit and plastic limit of the clayey samples were determined by Atterberg tests in accordance with ASTM D 4318. Chemical and mineralogical compositions of the clayey samples were determined by X-ray powder diffraction (XRD) using Philips PW 1010/80 diffractometer with graphite-filtered CuKα radiation. The XRD analysis was carried out on the <74-μm fraction of soil samples. Cation exchange capacity (CEC) and specific surface area (SSA) of clayey soil materials were determined using Ammonium Acetate (Chapman, 1965) and Ethylene Glycol Mono Ethylene Ether (Heilman et al., 1965), respectively. The pH values were determined with a pH meter (Thermo scientific Orion 5 star plus multifunction). In order to evaluate the microfabric structure of clayey materials, a sample was subjected to image analysis by using scanning electron microscope (SEM). Images generated were magnified 1000, 5000 and 10000 times by means of a SEM modeled JEOL JSM-6400 SEM. Before SEM examinations, the sample surfaces were coated with a thin layer (20 nm) of gold to

Table 1. Physical properties of samples.

Sample	Depth (m)	Density (mg/m^3)	Dry color	Wet color	Sand (%)	Silt (%)	Clay (%)
Central samples							
KCS1	0.0 - 1.2	2.56	5Y7/2	5Y6/3	18.3	20.5	61.2
KCS2	1.2 - 1.6	2.56	5Y7/1	5Y6/3	61.9	8.1	30.0
KCS3	1.6 - 3.0	2.55	5Y7/1	5Y6/3	15.7	16.3	68.0
KCS4	3.0 - 4.5	2.56	5Y6/2	5Y4/1	26.3	12.4	61.3
KCS5	4.5 - 6.0	2.56	5Y6/2	5Y4/2	18.5	16.3	65.2
KCS6	6.0 - 7.5	2.56	5Y7/2	5Y5/2	8.6	20.0	71.4
Northern samples							
KNS1	0.0 - 0.5	2.65	5Y5/1	5Y3/1	39.6	16.1	44.3
KNS2	0.5 - 1.3	2.59	5Y7/1	5Y6/2	26.5	16.3	57.2
KNS3	1.3 - 1.6	2.62	5Y6/2	5Y4/2	31.5	16.1	52.4
KNS4	1.6 - 1.8	2.56	5Y8/3	5Y7/4	14.3	24.4	61.3
KNS5	1.8 - 2.4	2.56	5Y6/2	5Y4/1	17.8	16.3	65.9
Southern samples							
KSS1	0.0 - 0.3	2.55	5Y6/3	5Y5/4	13.5	14.2	72.3
KSS2	0.3 - 0.7	2.55	5Y7/2	5Y6/3	6.2	16.3	78.5
KSS3	0.7 - 1.5	2.57	5Y8/1	5Y6/3	26.5	8.2	65.3
KSS4	1.5 - 1.8	2.56	5Y8/1	5Y7/2	22.5	8.2	69.3

obtain a conductive surface and to avoid electrostatic charging during examination. Water adsorption was determined test was carried out as described by ASTM D 570 at the Ataturk University laboratories. Also, concentrations of oxides of major elements and trace elements analyses were performed by X-ray fluorescence spectrometry on pressed powered pellets using a Philips PW 1480 at these laboratories.

RESULTS AND DİSCUSSİON

Table 1 presents the physical properties of identified clayey raw materials from Koprukoy (Erzurum) thermal area. Density of the clayey raw materials varied from 2.55 to 2.65 mg/m^3. The clayey material samples contain 30 to 78% clay and 8 to 24% silt. Frequently, the silt+clay fraction exceeded 95%. The grain-size analysis results revealed that the samples include high percentage of < 2 µm clay fraction. The smaller size of particles attributed to better thermal behavior, because the smaller the clay particle, the slower its cooling rate (Legido et al., 2007; Kalkan and Bayraktutan, 2008).

X-ray diffractograms showing mineral identified in the studied samples are presented on Figure 2, and summary of the XRD results were given in Table 2. The clayey raw materials consist of clay and non clay minerals. The XRD analysis results indicated that simectite was the most abundant clay mineral in all 15 samples. Other clay minerals identified were kaolinite, illite, mica and zeolite. Non clay minerals were quartz, calcite, plagioclase and feldspar. Although the Koprukoy clayey raw materials contain high amounts of micro and macro fossil shells and residual minerals, mainly quartz, plagioclase and feldspar, their higher smectite contents gave them thermal mud features (Cara et al., 2000; Karakaya et al., 2010).

It is mentioned in literature that the clayey raw materials including kaolinite and smectites are used in spa and beauty therapy, as are illite, interstratified illite/smectite and chlorite, and, on occasion, sepiolite and palygorskite. Besides phyllosilicates, these minerals contain Fe-Mn-(hydr)oxides and other associated phases such as calcite, quartz, and feldspars. The presence of these phases should be controlled, because the final product applied to the patient should have only the required and appropriate mineral properties for their use. The main properties of clay minerals determining their usefulness in spa and aesthetic medicine are: (i) softness and small particle size; (ii) appropriate rheological properties for the formation of a viscous and consistent paste; (iii) similarity in pH to that of the skin so as to avoid irritation or other dermatological problems; (iv) high sorption capacity; (v) high CEC; and (vi) high heat-retention capacity. Smectites fulfill many of the requirements for usage in spa and beauty therapy (Carretero, 2006).

The clayey raw materials had plasticity index between 27 and 52%. The liquid limit values were greater than 50%. The liquid limit values >50% indicate the presence of smectite. This positive correlation between liquid limit values and XRD results agrees with the suggestion of Means and Parcher (1963). When the liquid limit and plasticity index values were used to determine the degree

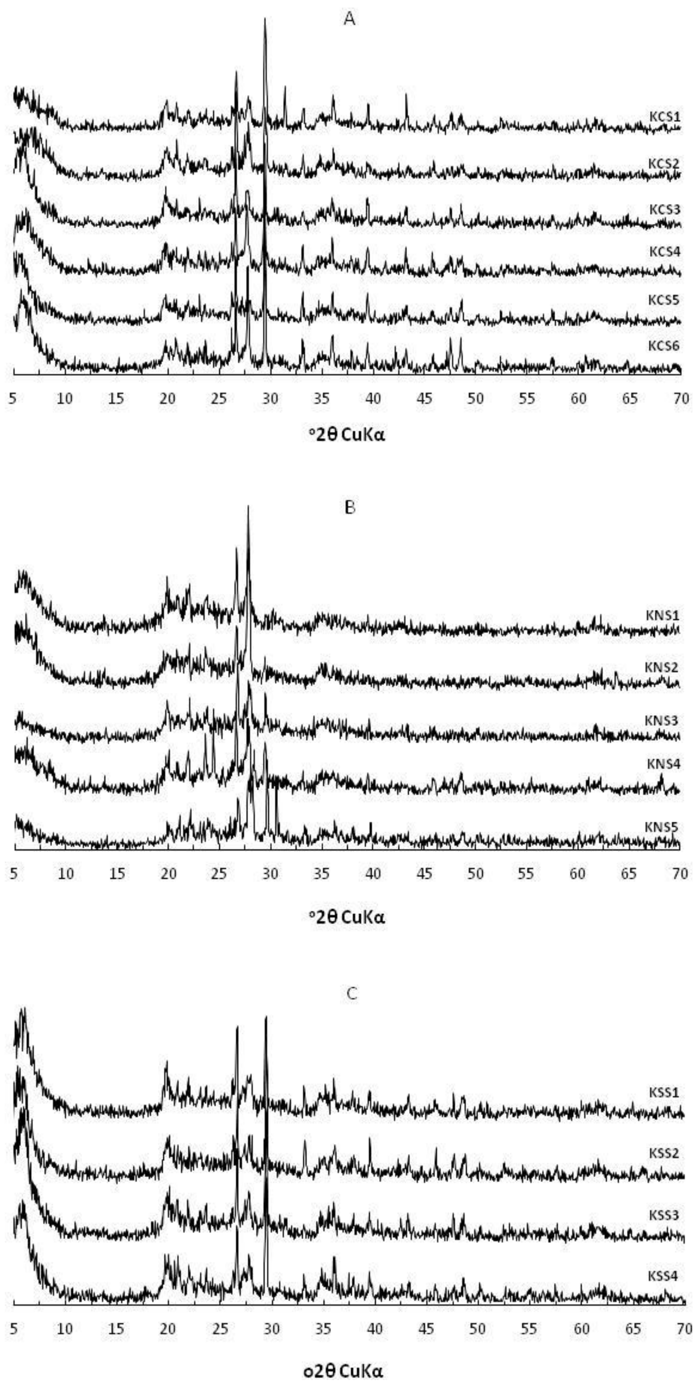


Figure 2. XRD pattern for (A) central, (B) Northern and (C) Southern samples.

of plasticity, high and very high plasticity was found, except one sample. As shown in Figure 3, the samples have fallen in the very high, high and moderately plastic areas on Casagrande's chart modified by Grabowska-Olszewska (1998) for the evaluation of plasticity of the thermal muds (Table 3).

Mechanical properties such as hardness, plasticity, grain size and swelling, affect handling properties of the peloid muds (Karakaya et al., 2010). The samples of clayey raw material had moderate, high and very high plasticity together with a high content of clay-size particles, high content of quartz and feldspars and high swelling. These properties may influence handling conveniences, as the clayey raw materials had smooth consistency and good thermal behavior due to a high level of hygroscopic water. As a result, the clayey raw

Table 2. Mineralogical properties of samples.

Samples	Clay minerals				Non clay minerals				
	S	K	I	Z	M	Q	C	P	F
Central samples									
KCS1	x				x	x	x	x	
KCS2	x	x	x			x	x	x	
KCS3	x	x			x	x	x	x	
KCS4	x					x	x	x	
KCS5	x				x	x	x	x	
KCS6	x				x	x	x	x	
Northern samples									
KNS1	x					x	x	x	
KNS2	x	x	x		x	x	x	x	
KNS3	x					x	x	x	
KNS4	x					x	x	x	
KNS5	x					x	x	x	
Southern samples									
KSS1	x					x	x	x	
KSS2	x			x		x	x	x	
KSS3	x					x	x	x	X
KSS4	x					x	x	x	

S: Smectite, K: Kaolinite, I: Illite, Z: Zeolite, M: Mica, Q: Quartz, C: Calcite, P: Plagioclase, F: Feldspar.

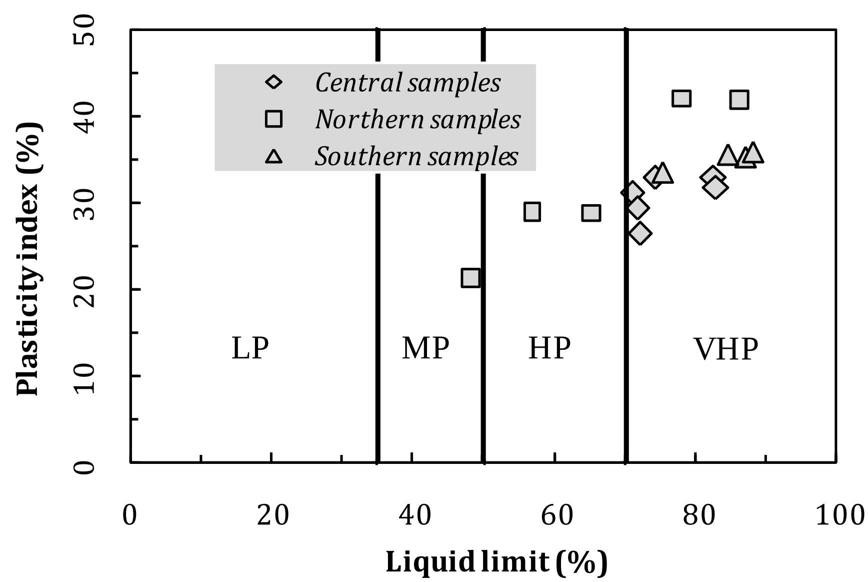


Figure 3. Casagrande's chart modified by Grabowska-Olszewska (1998) for the evaluation of plasticity of the samples (LP: Low plasticity, MP: moderate plasticity, HP: high plasticity, VHP: very high plasticity).

materials react with water to a maximal extent; and this was influenced by the presence of smectite, which is regarded as hydrophilic (Pajak-Komorowska, 2003; Kalkan, 2009, 2011). Pastes consisting of smectite/mineral water mixtures are the best materials for thermal pelotherapy applications (Morandi, 1999; Novelli,

Table 3. Consistency limits of samples.

Sample	Liquid limit (%)	Plastic limit (%)	Plasticity index (%)	Soil type
Central samples				
KCS1	71.0	31.1	39.9	VHPC
KCS2	82.6	32.9	49.7	VHPC
KCS3	74.2	33.0	41.2	VHPC
KCS4	82.9	31.8	31.8	VHPC
KCS5	71.7	29.3	42.4	VHPC
KCS6	72.1	26.5	45.6	VHPC
Northern samples				
KNS1	48.3	21.1	27.2	MPC
KNS2	56.7	28.8	27.9	HPC
KNS3	65.5	28.9	36.6	HPC
KNS4	78.3	42.1	36.2	VHPC
KNS5	86.5	41.7	44.8	VHPC
Southern samples				
KSS1	75.3	33.5	41.8	VHPC
KSS2	86.9	35.1	51.8	VHPC
KSS3	84.4	35.5	48.9	VHPC
KSS4	88.0	35.8	52.2	VHPC

VHPC: Very high plastic clay, HPC: high plastic clay, MPC: moderately plastic clay

2000). The high-swelling index and water limit (Laird, 1999), plasticity, specific surface (due to the high percentage of < 2 µm clay fraction) and exchange capacity of clayey raw materials including smectite make them suitable to improve the quality of peloid muds (Veniale et al., 2004).

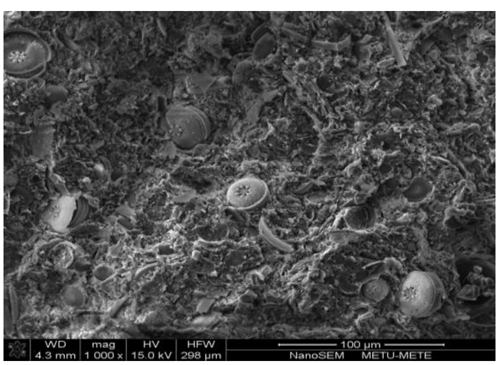
According to Kabata-Pendias and Pendias (2001) and Lopez-Galindo et al. (2007), kaolinite and illite present low CECs (3 to 22 and 20 to 50 meq/100 g, respectively) and SSAs (7 to 30 and 65 to 100 m^2/g, respectively); and smectites have high CEC (80 to 150 meq/100 g) and SSA (280 to 800 m^2/g). These properties are related to the interlayer spaces commonly occupied by hydrated exchangeable cations (Kabata-Pendias and Pendias, 2001; López-Galindo et al., 2007). Despite the high content of clay fraction and dominance of smectites in all studied samples, they still recorded CEC and SSA values lower than normal smectite values (Table 4). Some fragments of *Dreissensia* sp., *Gastropoda* sp. and *Congeria* sp. are observed in the clayey raw materials (Figure 4a to c). The high biogenic carbonate contents of these raw materials may have contributed to the lower CEC and SSA values (Table 3). The thermal characteristics of the clayey raw materials such as smectite clay mineral content, particle sizes, plasticity index and biogenic carbonate content make them suitable or the quantity of peloid muds in spite of low CEC and SSA values.

Table 5 shows the chemical analysis results of Koprukoy (Erzurum) raw clay materials determined by XRF analysis. Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, SiO_2, SO_3, K_2O and TiO_2 compositions are summarized on Table 5. Lack of correlation between SiO_2 and the other major elements, indicating that the SiO_2 contents, is mainly related to the abundance of quartz (Bianchini et al., 2002). Increased concentrations of SiO_2 reflect high quartz content and high CaO reflects calcite content. High percentage of SiO_2, Fe_2O_3, Al_2O_3 and MgO indicates the presence of smectite (Abduljauwad, 1993).

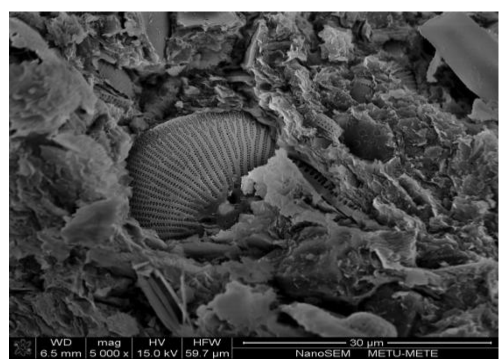
Trace elements identified in the samples are presented in Table 6. The CaO content may inhibit swelling, but nothing is reported in the literature regarding the effects this has on pelotherapy behavior (Harris, 1996). The trace element and Ca^{2+} content of peloid are important factors during pelotherapy, related to crossing the skin barrier and depositing in the bone. Ca is essential for developing and maintaining healthy bones and teeth; assists in blood clotting, muscle contraction and nerve transmission; and helps reduce risk of osteoporosis. Also, Ca, P, and Mg are fundamental for good state and performance of bones; and S helps to stabilize protein structures (Gomes and Silva, 2007). Biogenic carbonate is the active component, and the pH conditioner is responsible for the dissolution and corresponding liberation of Ca, Mg and other elements existing in the sand, making them available for adsorption through the skin and passage into the extra-cellular matrix (Gomes and Silva, 2007).

Table 4. Technological properties of samples.

Samples	Water absorption (ml/100 g)	CEC (meq/100 g)	Specific surface area (m^2/g)	Loss of hygroscopic water
Central samples				
KCS1	42.62	50.6	83.25	7.74
KCS2	44.52	50.8	85.21	7.54
KCS3	49.56	53.1	79.43	6.89
KCS4	43.02	50.3	78.35	7.24
KCS5	46.74	51.5	81.62	7.58
KCS6	45.67	52.8	79.23	7.42
Northern samples				
KNS1	27.58	42.8	53.08	5.28
KNS2	34.12	44.1	65.10	5.68
KNS3	28.97	43.2	68.54	5.44
KNS4	30.23	45.5	65.80	5.08
KNS5	34.18	47.6	66.02	5.66
Southern samples				
KSS1	36.33	42.1	57.02	5.78
KSS2	38.23	43.3	58.35	5.24
KSS3	34.28	40.1	56.22	5.12
KSS4	35.22	41.2	57.03	5.41



(a)



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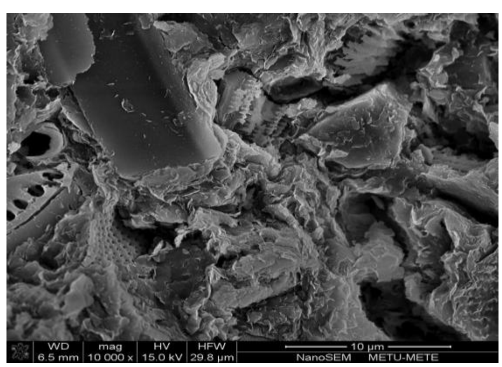

(c)

Figure 4. SEM image of clayey raw material (a) magnified 1000 times (b) magnified 5000 times and (c) magnified 10000 times.

Table 5. Concentration of oxides of major elements (in %) in samples.

Samples	Components											
	AL_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SiO_2	SO_3	K_2O	TiO_2	LOI	Total	Na_2O/ CaO
Central samples													
KCS1	8.55	5.39	14.09	1,98	1.03	0.94	44.49	0.22	1.02	0.42	21.82	99.95	0.218
KCS2	9.38	7.56	12.37	2,24	0.99	1.02	41.61	0.14	1.32	0.38	22.96	99.97	0.230
KCS3	6.81	4.40	34.04	2,02	0.62	0.92	31.22	0.28	0.98	0.32	18.32	99.93	0.183
KCS4	9.29	7.55	11.91	2,15	1.10	1.15	46.65	0.08	1.12	0.51	17.95	99.46	0.180
KCS5	10.02	8.36	14.02	2,32	1.17	1.20	46.41	0.13	1.42	0.39	14.38	99.82	0.144
KCS6	9.56	6.36	15.01	2,05	0.87	1.07	45.99	0.14	0.87	0.44	17.59	99,95	0.176
Northern samples													
KNS1	10.76	5.68	12.05	2.25	1.35	1.63	50.21	0.16	1.12	0.37	14.08	99.66	0.114
KNS2	11.09	6.06	12.45	2.2	1.31	1.55	52.19	0.16	1.03	0.41	11.41	99.86	0.105
KNS3	11.06	7.01	9.03	2.22	1.37	1.46	54.61	0.14	0.98	0.53	11.57	99.98	0.148
KNS4	8.92	6.81	11.96	1.81	0.90	1.10	54.94	0.16	0.88	0.46	11.49	99.43	0.075
KNS5	10.08	6.60	4.11	1.62	1.12	1.17	61.3	0.11	1.21	0.38	11.45	99.15	0.273
Southern samples													
KSS1	9.67	7.06	12.18	2.04	0.91	1.01	44.23	0.08	1.23	0.34	21.24	99.99	0.074
KSS2	10.3	6.92	10.03	2.29	0.88	0.94	47.43	0.07	1.03	0.37	19.6	99.86	0.085
KSS3	8.41	6.09	13.15	1.94	0.89	0.84	46.10	0.07	0.99	0.53	20.78	99.79	0.065
KSS4	9.68	7.70	13.26	2.44	1.01	1.03	46.52	0.12	0.97	0.42	16.80	99.94	0.073

The dense fragments of *dreissensia* sp., *gastropoda* sp. *and congeria* sp. observed in the clayey raw materials increase the biogenic carbonate. A high Na_2O/CaO ratio indicates the presence of swelling clay minerals, while a low ratio is typical for non-swelling clay minerals (Ravaglioli et al., 1989). Na_2O/CaO ratios in all samples were found to be lower than the swelling clay minerals because of high CaO contents caused by the biogenic carbonate (Cara et al., 2000).

Studies have shown fact that the occurrence of some microorganisms enhance therapeutic properties of the final peloid applied to the patient (Galzigna et al., 1996). According to Veniale et al. (2006) when the amount of smectite is too high, the growth of microorganisms, during peloid maturation, may be hindered due to the especial environment provoked for the physical-chemical properties of swelling clays. Dense algae growth indicates that the clayey raw materials contain abundantly smectite clay minerals (Veniale et al., 2006).

Figure 4a to c show the small size of the clay particles and their different microfabrics in SEM micrographs of the Köprüköy (Erzurum) clayey raw materials. Special mentioning deserves the smaller size of the saponite slightly crenulated (flaky) morphologies and its microporosity, which contrasted with the compact microfabric with cementation evidences of the smectite (Berbenni, 1965). As quoted by Yalcin and Gumuser (2000), smectite aggregates are composed of bent/folded, thin and subhedral lamellae (Figure 4). These loosely compacted, folded aggregates resemble Wyoming type (Grim and Guven, 1978) with “corn-flake” texture as described by Keller (1978). The smectite lamellae are associated with small amounts of short prismatic clinoptilolite (Yalcin and Gumuser, 2000; Yilmaz and Civelek, 2009).

Conclusion

The Erzurum (Köprüköy) clayey raw materials (NE Turkey) have been studied to determine their mineralogical and physicochemical properties and evaluation of their thermal mud characteristics. The following conclusions are derived from this investigation:

1. The grain-size analysis revealed that the samples the highest percentage of smaller than 2 µm. The smaller size of particles attributed to theirs better thermal behavior, since the smaller the clay particle.
2. It was observed that the dominant clay mineral was smectite and other clay minerals were kaolinite, illite, mica and zeolite. Non clay minerals identified were quartz, calsite, plagioclase and feldispare.
3. The degree of plasticity was high and very high except one sample which recorded moderate plasticity.
4. The dense fragments of *dreissensia* sp., *gastropoda* sp. and *congeria* sp. observed in the clayey raw materials increase the biogenic carbonate. Na_2O/CaO ratios in all samples were found to be lower than the swelling clay minerals because of high CaO contents caused by the biogenic carbonate.
5. Although, physicochemical properties such as CEC and SSA values were low because of very high biogenic

Table 6. Trace and RE elements (me/100 g) of samples.

Sample	Ca	K	Mg	Na	P	Al	B	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Se	Zn
Central samples																
KCS1	19.06	4.35	1.16	6.71	10.90	0.025	1.765	0.009	0.120	5.412	1.754	2.51	0.752	0.412	0.075	1.712
KCS2	15.66	2.31	7.54	6.32	28.80	0.021	1.815	0.012	0.103	5.036	2.120	2.41	0.921	0.358	0.086	1.254
KCS3	16.38	2.02	6.90	6.22	10.20	0.018	2.130	0.008	1.136	5.710	1.965	2.188	0.744	0.401	0.074	1.554
KCS4	15.79	1.49	5.51	5.74	9.50	0.076	0.853	0.009	0.119	5.235	2.003	3.717	0.865	0.371	0.072	1.972
KCS5	15.16	2.17	5.10	6.63	66.60	0.058	0.891	0.011	0.114	5.689	3.635	2.826	1.19	0.429	0.069	1.826
KCS6	16.03	1.87	5.47	5.88	19.21	0.043	1.672	0.008	0.176	5.452	2.861	3.124	0.913	0.523	0.083	1.762
Northern samples																
KNS1	10.34	3.10	2.20	2.39	21.00	0.048	0.612	0.051	0.135	5.959	8.274	3.42	9.097	0.645	0.048	3.246
KNS2	17.00	3.10	1.50	2.25	7.80	0.057	0.702	0.011	0.125	4.502	0.803	4.561	0.893	0.47	0.089	1.446
KNS3	15.20	2.66	1.09	2.53	16.80	0.048	0.719	0.005	0.130	6.319	1.038	2.97	0.851	0.495	0.079	2.461
KNS4	13.37	2.85	1.09	4.70	21.00	0.036	0.724	0.014	0.147	4.627	0.974	4.125	0.884	0.512	0.072	1.477
KNS5	15.70	2.92	1.30	5.37	12.40	0.051	0.688	0.007	0.152	5.124	0.887	3.12	0.896	0.41	0.063	2.11
Southern samples																
KSS1	15.38	1.78	2.20	1.65	7.80	0.046	1.322	0.001	0.124	6.284	1.026	0.664	0.393	0.432	0.085	1.141
KSS2	11.66	3.25	5.74	1.06	25.20	0.027	0.758	0.017	0.114	3.726	1.036	2.856	1.252	0.319	0.115	1.032
KSS3	10.08	2.67	2.43	3.86	40.10	0.051	0.804	0.025	0.125	4.324	1.389	3.384	1.93	0.342	0.115	1.239
KSS4	10.22	1.76	2.05	6.21	31.50	0.052	0.581	0.028	0.127	2.474	2.509	3.878	5.843	0.363	0.122	1.519

carbonate, other properties such as smaller grain size, high plasticity index, swelling index, smectite content and water absorption render the samples suitable for use as thermal mud.

6. Some properties such as CEC and SSA values decrease their suitability for thermal pelotherapic purposes, for this reason, it is recommended application of certain improvement or maturation processes. Finally, further research on the subject is recommended to improve the properties thermal pelotheraphy.

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