Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 12 (5): 480-485, 2012
ISSN 1812-5654 / DOI: 10.3923/jas.2012.480.485

The Suitability of Some Egyptian Smectitic Clays for Mud Therapy

E. El-Hinnawi and S.D. Abayazeed
National Research Centre, Dokki, Cairo Egypt

Abstract: The present study was carried out to assess the suitability of smectitic clays from Fayum, G. Hamza and G. Um Qamar, Egypt, for application in mud therapy. The textural, mineralogical and chemical composition of the Egyptian claystones showed that they are comparable to those of muds used in pelotherapy in several other countries (for example, Italy, Spain, Turkey and Portugal). The Egyptian claystones have good heat capacities and their pastes can be applied in different treatments. The trace elements present in the claystones, namely, As, Pb, Cu, Zn, Co, Ni and Cr are within the normal ranges of average natural mud and shale and they are of no significant concern for human health in mud applications.

Key words: Mud therapy, pelotherapy, heat capacity, smectite, heavy metals

INTRODUCTION

Historically, mud therapy has been used since Ancient Egyptian, Greek and Roman periods to cure skin, stomach and intestinal ailments, as well as for cosmetic purposes. With growing health tourism in several countries, the feasibility of using mud in spas received much attention over the past few decades (Mascolo *et al*., 1999; Carretero, 2002; Veniale *et al*., 2004; Carretero *et al*., 2006).

There are two main types of mud therapy: geotherapy, in which virgin clays are mixed with water and then applied to different parts of the body; and pelotherapy, in which the virgin clays are mixed with normal water, sea water or mineral water and left to mature for months to the so-called "peloids" and then applied to the body in spas. The effects of mud therapy in treating several diseases have been demonstrated by experimental and clinical data. The mud treatment helps in alleviating the pain and improving the functional status of the patients with rheumatic and arthritic conditions and the antibacterial and anti-inflammatory action of the mud has a beneficial effect on skin diseases (Von Tubergen and van der Linden, 2002; Flusser *et al*., 2002; Codish *et al*., 2005; Pittler *et al*., 2006; Odabasi *et al*., 2008; Stojkovic and Sremcevic, 2011).

In spas, the muds used have generally been subjected to maturation. The resulting solid-liquid mixture was defined by the International Society of Medical Hydrology as peloid and the treatment with this mud has been referred to as pelotherapy. In this respect, the word peloid was derived from the Greek word pelos which means mud. However, the term peloid, as used in mud therapy, should not be confused with the same term introduced by Mckee and Gutschick (1969) in sedimentary carbonate petrology. In the latter, a peloid is a sand-sized grain with an average size of 100-500 μm, composed of microcrystalline carbonate. (Tucker *et al*., 1990; Flugel, 2004). To avoid such confusion, the present authors use the term mud therapy rather than pelotherapy.

Not all muds can be used for mud therapy. The suitability of the mud depends on its physico-chemical properties and mineralogical composition. . The clay mineral content and type determine desirable properties such as high swelling , high specific surface area and cation exchange capacity and high specific heat, (Cara *et al*., 2000a, b). The mud should also meet certain requirements of purity, in particular microbial and toxic metal contamination (Summa and Tateo, 1998; Vreca and Dolenec, 2005). Some recent investigations showed the necessity of studying the geochemical composition of the muds used in therapy due to their toxicity and possible resorption through the skin (Summa and Tateo, 1999; Tateo *et al*., 2009).

The present research gives the results of a study carried out to examine the suitability of smectitic clays, from two main localities in Egypt, for application in mud therapy.

MATERIALS AND METHODS

Nine composite samples of smectitic clays were collected from Fayum Depression and Gebel Hamza-Gebel Um Qamar area along the Cairo-Ismailia Road (Fig. 1). The samples collected from Fayum Depression were from the interbedded claystone, siltstone and quartz sandstone facies of Qasr El-Sagha Formation of Late Eocene age.

Corresponding Author: E. El-Hinnawi, National Research Centre, Dokki, Tahrir Steet, Cairo, Egypt

Those samples collected from Gebel Hamza-Gebel Um Qamar area were from the claystone-sandstone-carbonate facies of Lower Miocene deposits.

The textural characteristics of the samples were determined by wet sieving and the pipette method (Tucker, 1988) and the percentages of sand, silt and clay fractions were plotted in the triangular diagram of Folk (1974), to classify the samples.

The mineralogical composition of the samples was determined by X-ray powder diffraction (XRD) analysis, according to the method described by Poppe *et al*. (2001). Two types of analyses were made: the first for the bulk powdered samples to determine the clay and non-clay minerals present and the second analysis for the determination of clay minerals present in the separated clay fraction (<2 μm).

The chemical composition of the mud samples (major and selected trace elements) was determined using Energy Dispersive X-ray Fluorescence (EDXRF) at the Mineralogical Institute, Karlsruhe, Germany.

The determination of the thermal characteristics of the smectitic clay samples was carried out by the preparation of pastes using 100 g of each sample and distilled water. The mixture was stirred until a suitable homogenous paste was obtained. A thermometer probe was inserted in the paste and was connected to a digital meter for recording the temperature. The container with the paste was placed in a water bath and heated until it reached 60°C. The container was then removed and the paste left to cool; the temperature was recorded every 5 min until it reached 30°C. The cooling curves of the samples were then defined between 60 and 30°C.

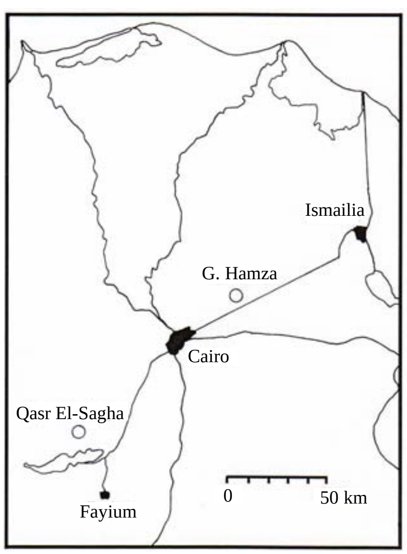

Fig. 1: Location map

RESULTS

Textural characteristics: Table 1 gives the results of granulometric analyses and indicates that the samples are mainly composed of clay and silt, with minor quantities of sand. According to Folk's classification (Fig. 2), the samples are classified as claystone, with generally more than 75% clay. It should be noted, however, that some other samples from the localities studied are either mudstones or sandy claystones. For the purpose of the present study we selected those layers that are composed mainly of claystone.

Mineralogical composition: The XRD analyses of the whole samples revealed that they are composed mainly of clay minerals, with minor quantities of quartz and in some cases carbonate minerals (calcite). The clay minerals present are smectite and kaolinite, with minor quantities of illite (Table 1).

Table 1: Texture and mineralogy of smectitic clays

	Texture (%)			Estimated clay minerals (%)*		
Sample	Sand	Silt	Clay	Smectite	Illite	Kaolinite
QS1	2.5	8.9	88.6	58.0	16.0	26.0
QS2	1.3	22.4	76.3	54.0	6.0	40.0
QS3	0.5	16.4	83.1	52.0	10.0	38.0
H1	0.6	20.0	79.4	64.0	4.3	31.7
H2	0.2	13.3	86.5	39.8	1.6	58.6
H3	0.2	16.6	83.2	46.3	3.2	50.5
UQ1	0.1	21.2	78.7	68.8	1.3	29.9
UQ2	1.3	21.9	76.8	69.3	0.8	29.9
UQ3	0.2	31.4	68.4	69.7	1.3	29.0

*In clay fraction (<2 μm), QS: Qasr El-Sagha samples (Fayum depression), H: Gebel Hamza samples, UQ: Um Qamar samples

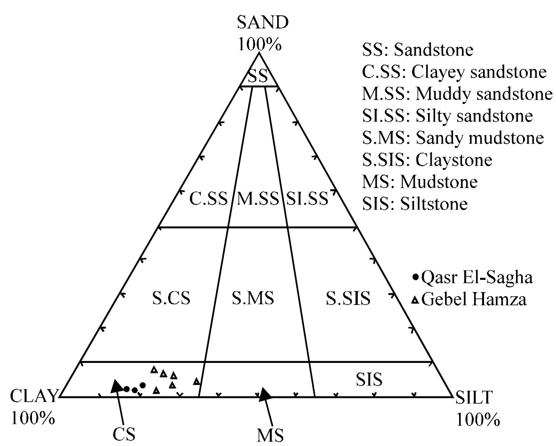

Fig. 2: Triangular diagram of folk (G Hamza samples include those of Um Qamar)

Table 2: Chemical composition of smectitic claystone samples

	QS1	QS2	QS3	H1	H2	H3	UQ1	UQ2	UQ3	Ave mud	Ave. Shale
SiO_2	56.05	57.63	54.64	52.9	48.54	50.87	52.16	53.24	51.98	63.96	58.39
Al_2O_3	23.01	20.82	22.41	20.99	25.2	24.45	24.51	23.9	22.67	19.45	15.12
Fe_2O_3	3.64	4.82	3.96	8.55	9.66	8.36	7.13	7.17	8.87	7.29	6.75
MnO	0.1	0.1	0.1	0.04	0.03	0.04	0.03	0.03	0.08	0.11	0.11
MgO	2.25	1.7	1.77	1.86	1.38	1.32	1.75	1.53	1.75	2.32	2.49
CaO	1.96	1.77	3.3	0.59	0.49	0.48	0.47	0.63	0.61	1.3	3.09
Na_2O	1.62	2.54	3.59	1.13	1.3	1.23	1.39	1.26	1.33	1.2	1.29
K_2O	1.17	0.5	0.15	1.44	1.02	1.1	1.23	1.22	1.25	3.86	3.21
TiO_2	0.2	0.14	0.15	1.65	1.88	2.02	1.55	1.52	1.57	1	0.77
P_2O_5	0.11	0.11	0.09	0.09	0.18	0.14	0.06	0.15	0.11	0.17	0.16
LOI	9	8.96	9.58	8.8	10.22	9.86	9.58	9.26	9.67		
Total	99.11	99.09	99.74	98.04	99.07	99.87	99.86	99.91	99.89		
Trace elements (ppm)											
As	2	5	5	3	5	6	5	5	4	11	13
Co	19	12	13	1	14	22	24	38	32	20	19
Cr	90	75	70	158	146	167	174	171	180	100	90
Cu	45	40	40	47	12	39	28	32	28	50	45
Ni	68	60	66	95	41	66	82	64	92	60	50
Pb	20	15	12	28	8	6	6	5	5	20	20
Zn	95	82	71	92	57	82	90	80	93	85	95

Fe_2O_3: Total iron Average mud after (McLennan, 1995), Average shale after (Turekian and Wedepohl, 1961), QS: Qasr El-Sagha samples (Fayum depression), H: Gebel Hamza samples, UQ: Um Qamar samples

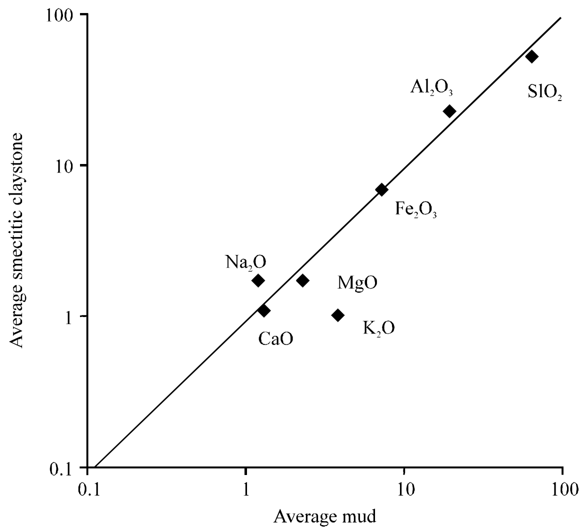

Fig. 3: Relationship between average major elements in smectitic claystones and average mud

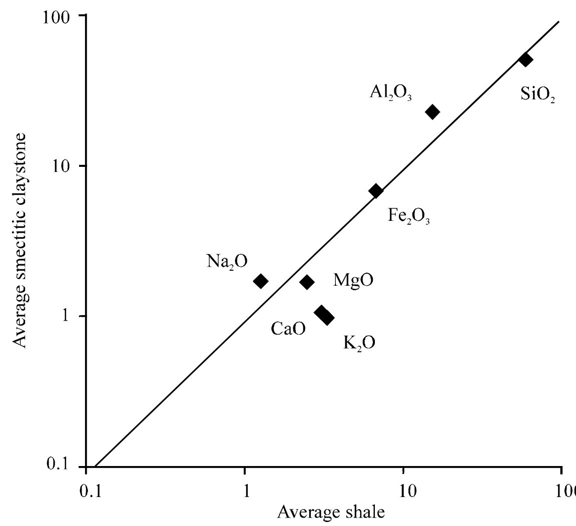

Fig. 4: Relationship between average major elements in smectitic claystones and average shale

Chemical composition: Table 2 gives the results of the chemical analyses of the studied smectitic claystone samples, compared to average mud (McLennan, 1995) and average shale (Turekian and Wedepohl, 1961). The SiO_2 content in the samples varies between 48.54 and 57.63% and is, on average, lower than that in average mud and average shale. The Al_2O_3 varies between 20.80 and 25.20%, higher, on average, than that in average mud and average shale (Fig. 3, 4). This is attributed to the fact that the smectitic claystone samples contain a higher content of clay minerals and a lower content of quartz than the average mud or average shale. The claystone samples contain, on average, a lower percentage of K_2O, due to their lower content in illite. They also have a lower MgO and CaO and a higher Na_2O than the average mud or average shale.

The Na_2O/CaO ratio in the smectitic claystone samples varies between 0.83 and 2.96 and is generally higher than 1.0. For comparison, the thermal muds of some spas in Turkey have a Na_2O/CaO ratio of 0.02-0.58 (Karakaya *et al*., 2010). A high Na_2O/CaO ratio indicates the presence of swelling 2:1 clay minerals ($1<Na_2O/CaO<3$), while a low ratio ($Na_2O/CaO<1$) is typical of non-swelling 2:1 clay minerals.

Table 2 gives also the concentration of some selected trace elements in the studied smectitic claystones and

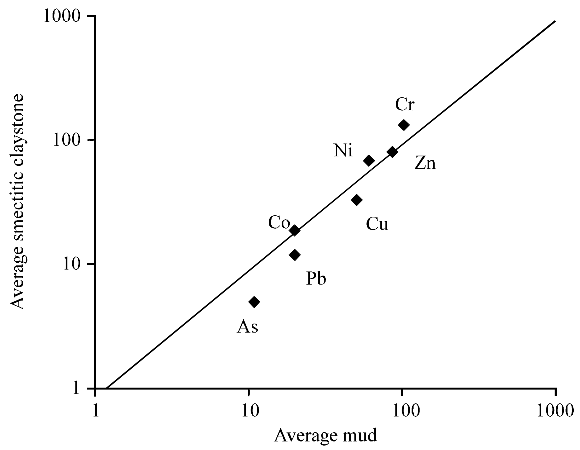

Fig. 5: Relationship between average trace elements in smectitic claystones and average mud

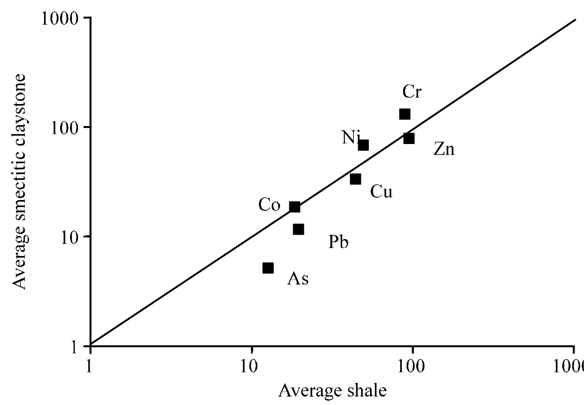

Fig. 6: Relationship between average trace elements in smectitic claystones and average shale

Fig. 5 and 6 show a comparison between the average trace elements determined and those present in average mud and average shale, respectively. The figures indicate that As, Pb and Cu are lower in the smectitic claystones than in average mud or average shale, whereas Cr and Mi are slightly higher.

Cooling kinetics: Figure 7-9 show the cooling kinetic curves of the claystones from Qasr El-Sagha, Gebel Hamza and Um Qamar, respectively. All curves show a negative correlation between temperature and cooling time, with an average R^2 of 0.9. Using the equations introduced by Cara *et al*. (2000b), the heat capacity (C_P) of the pastes and the temperature (T_{20}) after 20 min of cooling were calculated (Table 3). The results obtained are closely similar to those of other thermal muds from Sardinia (Cara *et al*., 2000b) and to those of matured peloids from Italy (Veniale *et al*., 2004).

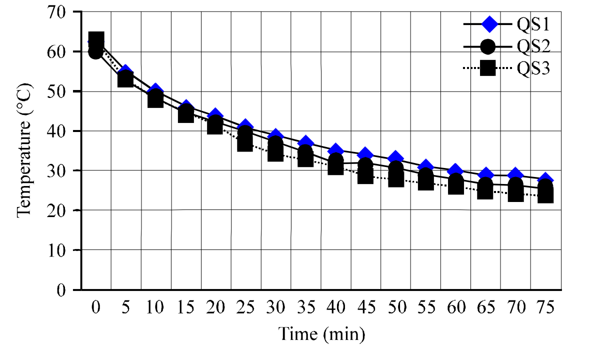

Fig. 7: Cooling kinetic curves of Qasr El-Sagha claystones

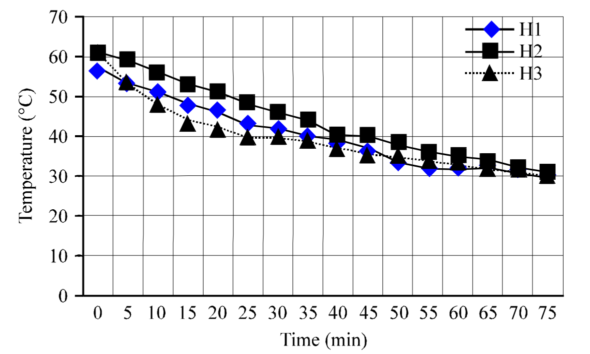

Fig. 8: Cooling kinetic curves of Hamza claystones

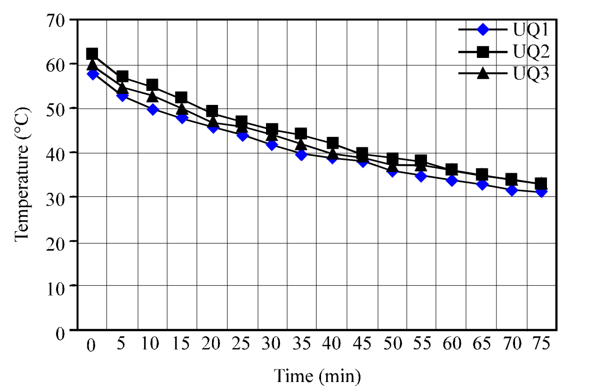

Fig. 9: Cooling kinetic curves of Um Qamar claystones

Table 3: Moisture content and calculated heat capacity and T_{20} of the smectitic claystones

Sample	Water (%)	C_P	T_{20}
QS1	66.7	2.91	32.46
QS2	55.6	2.48	31.57
QS3	50	2.26	30.1
H1	52.4	2.35	31.07
H2	52.4	2.35	31.07
H3	52.4	2.35	31.07
UQ1	52.4	2.35	31.07
UQ2	52.4	2.35	31.07
UQ3	52.4	2.35	31.07

C_P: Heat capacity of mud paste, T_{20}: Temperature reached by the mud paste after 20 min of application, QS: Qasr El-Sagha samples (Fayum depression), H: Gebel Hamza samples, UQ: Um Qamar samples

DISCUSSION

The smectitic clays of Fayum, G. Hamza and Um Qamar are mainly composed of clay with less amounts of silt and minor quantities of quartz. The mineralogical and chemical composition of these claystones are comparable to those of muds used for mud therapy, for example the muds from Sardinia (Cara *et al*., 2000a) and those from Croatia (Mihelecic *et al*., 2011). The Egyptian claystones have also comparable cation exchange capacity and specific surface area (Abayazeed and El-Hinnawi, 2011), In addition, the Egyptian claystones have generally similar heat capacities to those used in mud therapy.

A particular concern in using mud for mud therapy has focused on the concentration of some trace elements, particularly heavy metals, in the muds (Mascolo *et al*., 1999; Tateo *et al*., 2009; Carretero *et al*., 2010; Rebelo *et al*. 2011). These metals have been classified into three classes (Rebelo *et al*., 2011): Class 1 includes Cd, Pb and As, elements that should be essentially absent because they are known as human toxicants or environmental hazards; Class 2 includes Mo, Ni,V, Cr,Cu and Mn, elements that should be limited in pharmaceuticals and have less toxicity than those in Class 1. Class 3 includes those elements that may be present as impurities in some cosmetic products (e.g., Ba, Se, Zn and Sb). Even though Zn has no significant toxicity, Sb is included as an element of primary toxicological concern in cosmetics together with Pb, As, Cd and Hg.

The analyzed trace elements in the Egyptian claystones exhibited normal values for average mud and average shale (Fig. 5, 6). The slightly higher levels of Cr and Ni. are due to variations in lithology and are within the natural normal ranges of these elements. For comparison, the Dead Sea black mud used for mud therapy contains 24-26 ppm Co, 108-114 ppm Pb and 73-108 ppm Zn (Khlaifat *et al*., 2010), generally higher than those found in Egyptian claystones. Although, on average, the latter clays contain 136 ppm Cr, which is higher than that in Dead Sea black mud (40-66 ppm, according to Momani *et al*. (2009), Portuguese muds contain higher Cr , up to 196 ppm (Rebelo *et al*., 2011).

In mud therapy, the mud can be applied to different parts of the body or on the whole body by means of masks and poultices, or even in bathing the body partly or totally, for therapeutic or cosmetic purposes. In most cases the mud is applied hot. In all the applications an interface between the mud and the skin is formed in which perspiration plays an important role. In this interface an exchange of chemical elements may take place. Ions and other compounds may pass from the mud to the skin and enter the blood stream. Conversely, ions and other substances may pass from the skin into the mud. In either case, sweat is the interface between mud and skin. Tateo *et al*. (2009) studied the in-vitro percutaneous migration of chemical elements from a thermal mud mixed with mineral water. They found that the doses of Cr, Cu, Ni, Pb and Zn supplied to the body, after 20 min of treatment, are far below the daily dietary intakes recommended for these elements by the World Health Organization. Carretero *et al*. (2010) studied the mobility of elements in interaction between artificial sweat and muds used in Spanish spas. They found that the heavy metals Cu, Pb, Ni and Zn are ab/adsorbed from the sweat to the mud leading in most cases to their removal from the leached extract. Other elements, such as Cd, Co and Cr are generally not leached. Accordingly and due to the fact that the trace elements in the Egyptian claystones are generally lower than those encountered in other muds used for mud therapy, these trace elements are of no concern from the health point of view in mud treatments.

CONCLUSION

The mineralogical, chemical and thermal characteristics of the Egyptian claystones from Fayum, G. Hamza and G. Um Qamar are comparable tp those of muds used for pelotherapy in Italy, Spain, Portugal and Croatia. The Egyptian claystones have, in general, lower concentrations of heavy metals than other muds, for example the Dead Sea black mud and the presence of such elements in the claystones is of no health concern in mud treatments.

The Egyptian claystones can be used as virgin clays, mixed with water, or mineral water, or can be subjected to maturation by mixing with sea water or other combinations, according to their therapeutic use.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to Prof. Dr. Doris Stüben, Leader of the Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, Germany, for her kind support. Our thanks go also to Dr. U. Kramar of the same Institute for his assistance in carrying out the chemical analyses in Karlsruhe.

REFERENCES

Abayazeed, S.D. and E. El-Hinnawi, 2011. Characterization of Egyptian Smectitic clay deposits by methylene blue adsorption. Am. J. Applied Sci., 8: 1282-1286.

Cara, S., G. Carcangiu, G. Padalino, M. Palomba and M. Tomanini, 2000a. The bentonites in pelotherapy: chemical, mineralogical and technological properties of materials from Sardinia deposits, Italy Applied Clay Sci., 16: 117-124.

Cara, S., G. Carcangiu, G. Padalino, M. Palomba and M. Tomanini, 2000b. The bentonites in pelotherapy: thermal properties of clays pastes from Sardinia deposits, Italy. Applied Clay Sci., 16: 125-132.

Carretero, M.I., 2002. Clay minerals and their beneficial effects upon human health. Applied Clay Sci., 21: 155-163.

Carretero, M.I., C.F.S. Gomes and F. Tateo, 2006. Clays and Human Health. In: Handbook of Clay Science, Bergaya, F., B.K.G. Theng and G. Lagaly, (Eds.). Elsevier Science, USA.

Carretero, M.I., M. Pozo, J.A. Martin-Rubi, E. Pozo and F. Maraver, 2010. Mobility of elements in interaction between artificial sweat and peloids used in Spanish spas. Applied Clay Sci., 48: 506-515.

Codish, S., M. Abu-Shakra, D. Flusser, M. Friger and S. Subenik, 2005. Mud compress therapy for the hands of patients with rheumatoid arthritis. Rheumatol. Int., 25: 49-54.

Flugel, E., 2004. Microfacies of Carbonate Rocks, Analysis, Interpretation and Application. Springer-Verlag, Berlin, pp: 976.

Flusser, D., M. Abu-Shakra, M. Friger, S. Codish and S. Sukenik, 2002. Therapy with mud compresses for knee osteoarthritis: Comparison of natural mud preparations with mineral-depleted mud. J. Clin. Rheumatol., 8: 197-203.

Folk, R.L., 1974. Petrology of Sedimentary Rocks. 2nd Edn., Hemphill Publishing Co., Austin, Texas, ISBN: 0914696033, pp: 184.

Karakaya, M.C., N. Karakaya, S. Sarýoglan and M. Koral, 2010. Some properties of thermal muds of some spas in Turkey. Applied Clay Sci., 48: 531-537.

Khlaifat, A., O. Al-Khashman and H. Qutob, 2010. Physical and chemical characterization of Dead Sea mud. Mater. Charact., 61: 564-568.

Mascolo, N., V. Stumma and F. Tateo, 1999. Characterization of toxic elements in clays for human healing use. Applied Clay Sci., 15: 481-500.

McLennan, S.M., 1995. Sediments and Soils: Chemistry and Abundances. In: Rock Physics and Phase Relations, A Handbook of Physical Constants. Aherns, T.J. (Ed.). America Geophysical Union, USA., pp: 8-19.

Mckee, E.D. and R.C. Gutschick, 1969. History of the Redwall limestone of Northern Arizona. Geological Society of America, USA., Pages: 726.

Mihelecic, G., G. Kniewold, G. Ivanisevic, V. Mihecic and N. Vdovic, 2011. Physico-chemical characterization of the peloid mud from Morinje Bay (Eastern Adreiatic coast, Croatia), suitability for use in balneotherapy. Environ. Geochem. Health, 10.1007/s10653-011-9434-y.

Momani, K., T. El-Hasan, S. Auayleh and K. Al-Nawaysch, 2009. Heavy Metals Distribution in the Dead Sea Black Mud, Jorden. Journal of Earth and Environmental Science, Jourdan, pp: 50-59.

Odabasi, E., M. Turan, H. Erdem and F. Tekbas, 2008. Does mud pack treatment have any chemical effect? A randomized controlled clinical study. J. Altern. Compliment Med., 14: 559-565.

Pittler, M.H., M.Z. Karagulli, M. Karagulli and E. Ernst, 2006. Spa therapy and balneotherapy for treating low back pain. Rheumatology, 45: 880-884.

Poppe, L.J., V.F. Paskevich, J.C. Hathaway and D.S. Blackwood, 2001. A laboratory manual for X-Ray power diffraction. U.S. Geol. Survey.

Rebelo, M., C. Viseras, A. Lopez- Galiando, F. Rocha and E. Ferreira da Silva, 2011. Characterization of Portuguese geological materials to be used in medical hydrology. Applied Clay Sci., 51: 258-266.

Stojkovic, N. and N. Sremcevic, 2011. Banja Koviljaca's sulphuric peloid application in children. Med. Data Rev., 3: 85-92.

Summa, V. and F. Tateo, 1998. The use of pelitic raw materials in thermal centres: Mineralogy, geochemistry, grain size and leaching tests. Examples from the Lucania area southern Italy. Applied Clay Sci., 12: 403-417.

Summa, V. and F. Tateo, 1999. Geochemistry of two peats suitable for medical uses and their behavior during leaching. Applied Clay Sci., 15: 477-489.

Tateo, F, A. Ravaglioli, C. Andreoli, F. Bonina and V. Coiro *et al*., 2009. The *in-vitro* precuntaneous migration of chemical elements from a thermal mud for healing use. Applied Clay Sci., 44: 83-94.

Tucker, M.E., 1988. Techniques in Sedimentology. Blackwell Sci., Oxford, UK., pp: 394.

Tucker, M.E., V.P. Wright and J.A.D. Dickson, 1990. Carbonate Sedimentology. Blackwell Scientific Publications, Oxford, UK.

Turekian, K.K. and K.H. Wedepohl, 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull., 72: 175-192.

Veniale, F., E. Barberis, G. Cacangin, N. Morandi, M. Setti, M. Tamanini and D. Tessier, 2004. Formulation of muds for pelotherapy: Effects of maturation by different mineral waters. Applied Clay Sci., 25: 135-148.

Von Tubergen, A. and S. van der Linden, 2002. A brief history of spa therapy. Ann. Rheum. Dis., 61: 273-275.

Vreca, P. and T. Dolenec, 2005. Geochemical estimation of copper contamination in the healing mud from Makirina Bay, central Adriatic. Environ. Int., 31: 53-61.