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Textural, Mineralogical and Geochemical Assessment of the Pikrolimni Lake Sediments (Kilkis district, Northern Greece) and suitability for use in pelotherapy

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Mud therapy has been used since ancient periods for medical or cosmetic purposes. Pelotherapy is the application of thermal muds (peloids) for recovering muscle-bone-skin pathologies (Veniale et al. 2007). Peloid muds are fine grained sediments, produced by different geological and biological processes. Because of their positive and beneficial effect on human organisms their mixture with water could often be used for mud baths and cataplasms. Nowadays, pelotherapy is being more and more focused on specific pathologies and treatments. However, not all muds can be used for mud therapy, whereas natural occurrences of suitable thermal muds are going exhausted. To be suitable for pelotherapy, certain qualities of peloids are necessary. Textural, mineralogical and geochemical characteristics of a virgin mud are critical factors ruling its quality for use as peloid mud in pelotherapy. Special attention was given to potentially toxic elements (PTE) namely As, Cd, Cr, Cu, Hg, Ni, Pb, Zn etc., because of their hazardous effect on human health (Carretero et al., 2010; Rebelo et al., 2011).

The present research was conducted on the Pikrolimni Lake sediments (PLS). Pikrolimni Lake is located in the Kilkis district, near Thessaloniki (23 km), in northern Greece. It is a small shallow lake up to 1.5 m depth, and it is well known as a pelotherapy center. PLS are used for the preparation of peloid mud, but no detailed data exist on their characteristics.

The aim of this investigation was to assess the texture, mineralogy and geochemistry of PLS. Chemical results were compared with reported Earth's upper crust average shale (Li, 2000) as well as with different muds used for medical purposes. The index of geo-accumulation (Igeo) and the iron normalized enrichment factor (EF) were used for the characterization of PTE contamination levels. The results of this investigation aim at helping to develop suitable processes for making the PLS suitable for therapeutic uses.

Three composite samples were prepared by mixing of least 10 sub-samples collected from representative bottom surfaces 5x10 m of the lake. Portions of the sediment samples were used for grain size, mineralogical and geochemical analyses. The grain size composition was performed according to the ASTM D 422-63 and ASTM 2217-85.

X-ray powder diffraction (XRD) analysis was used for the study of the mineralogical composition of the sediments. Bulk samples and the separated clay fraction (<2μm) in oriented, glycolized and heated samples were used. The major and minor element oxides were determined by X-ray fluorence analysis (XRF), whereas the concentrations of PTE were determined by inductively coupled plasma mass spectrometry (ICP-MS). All the analytical work was conducted at the Laboratories of the Institute of Geology and Mineral Exploration (IGME).

Textural analyses showed that the sediment samples are composed of 73.10% sand, 23.62% silt and 3.27% clay, and are classified as sandy loamstones (Curtis 2005) This means that a sieving is necessary to improve the quality of the sediments for application in pelotherapy.

XRD analyses revealed that the PLS are composed of high average quantities of quartz (59.3%) and clay minerals (19.7%), followed by muscovite (12.0%), albite (8.0%) and carbonates (1%). The clay minerals present are mainly kaolinite, with minor montmorilonite, and illite.

The chemical composition of PLS showed an increased SiO_2 content varying between 63.44 and 70.35% (average value 66.97%), and a lower Al_2O_3 varying between 8.86% and 12.60% (average value 10.72%), expressing the mineralogical composition of them. In comparison with the chemical composition of the average shale the PLS have significantly higher SiO_2 and lower Al_2O_3 (58.39% and 15.12%, respectively). This is attributed to the fact that the PLS samples have a larger content of quartz and a lower content of clay minerals. They also have lower Fe_2O_3 (3.41%) and higher Na_2O (2.61%) than the average shale (6.75% and 1.29%, respectively. A lower percentage of K_2O (1.60%) in PLS, in relation to that of the average shale (3.21%), is due to their lower content of illite. The concentrations of MnO, MgO, TiO_2 and P_2O_5 is comparable with those referred for the average shale. The Na_2O/CaO ratio is<1, confirming the presence of the typical non-swelling 2:1 clay minerals (El-Hinnawi and Abayazeed, 2012).

The analyzed PTE in PLS (Table 1) were found to be higher for Pb, As, Ni, Cr and Zn and lower for Co and Cu in comparison to average shale. The calculated *Igeo* values, on the basis of average shale composition, showed moderate contamination for Pb and As and no contamination for Ni, Zn, Cr, Co, Cu for the PLS. The *EF* values for Ni, Zn, Cr, Co, and Cu ($EF \leq 1$) denoted no enrichment that is a natural origin of them. The minor enrichment found for As and Pb ($1 < EF < 3$), must be associated with anthropogenic activities. Pb and As were classified into the first group of heavy metals that should be essentially absent from peloids because they are known as human toxicants or environmental hazardous (Rebelo *et al*., 2011). However, many examples of peloid muds applied to pelotherapy are referred to contain higher levels of these heavy metals (Quintela *et al*., 2012; Rizo *et al*., 2013).

In conclusion, on the basis of the texture the PLS can be used as virgin clays in pelotherapy only after sand size particles could be separated by sieving, before any potential application. It is an advantage for PLS that the most PTE are within normal ranges. The minor enrichment of PLS in Pb and As is probably of no significant concern for human health in case of their application in pelotherapy.

Table 1. Summary of heavy metals data for the Pikrolimni Lake sediments

Trace elements	Range (mg/kg)	Average (mg/kg)	Average shale	EF	Description of enrichment	Igeo	Description of contamination
As	24-42	33,33	13	1,92	Minor enrichment	0,77	Moderate
Co	9-12	10,67	19	0,42	No enrichment	-1,42	Uncontaminated
Cr	80-92	85,67	90	0,71	No enrichment	-0,66	Uncontaminated
Cu	29-33	31,00	45	0,51	No enrichment	-1,12	Uncontaminated
Ni	46-52	49,00	50	0,73	No enrichment	-0,61	Uncontaminated
Pb	30-35	32,67	20	1,22	Minor enrichment	0,12	Moderate
Zn	85-110	95,33	95	0,75	No enrichment	-0,58	Uncontaminated

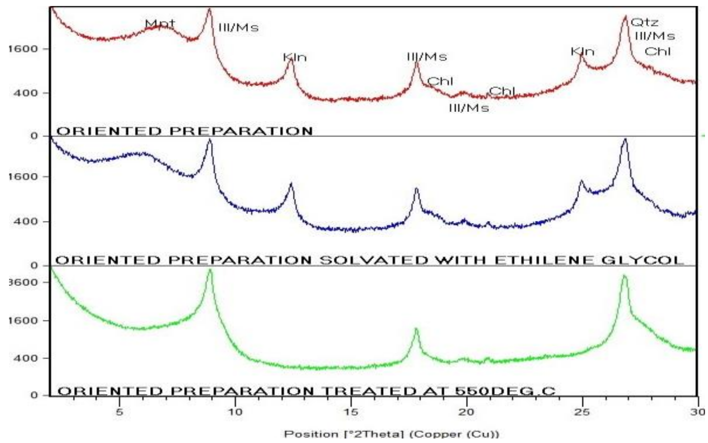

Fig.1. XRD patterns of Pikrolimni Lake sediments (Ill/Ms-Illite/Muscovite, Kln-Kaolinite, Mnt-Montmorillonite, Chl-Chlorite, Q-Quartz).

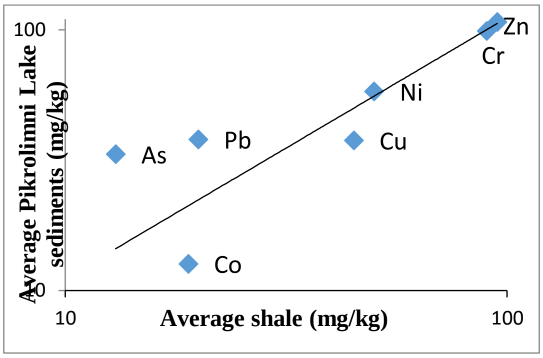

Fig. 2, Relationship between average trace elements in PLS and average shale

A further investigation is needed to study the concentration of these metals in a derivative peloid mud from the PLS and to determine the mobility and bioavailability of the metals. These properties are among the most important for the suitability of a peloid mud for pelotherapy.

Acknowledgements

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