



CHARACTERIZATION OF SOME THERAPEUTIC MUDS COLLECTED AT DIFFERENT SITES IN ROUMANIA

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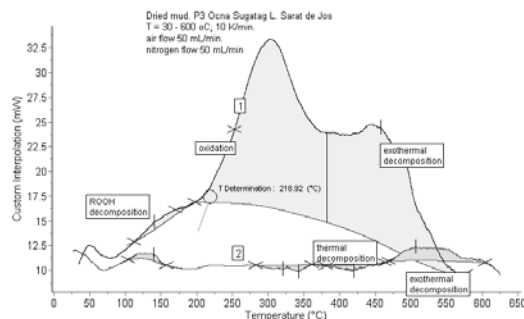
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The elemental composition of several therapeutic muds collected at different sites in Roumania has been determined by X-Ray Fluorescence (XRF) and Instrumental Neutron Activation Analysis (INAA). Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) spectroscopy was related to optical microscopy and Differential Scanning Calorimetry (DSC) data for characterization the thermal behavior was used. To assess the organic content, a gravimetric analysis has been performed before and after the DSC measurement in air atmosphere up to 600 °C. The results indicate significant differences, depending on the region, between the samples in terms of both composition and structure.



INTRODUCTION

In spite of reduction or removal from service for the last twenty years of industries which lead to soil pollution with heavy metals such as mining, metallurgy or chemical industry, and considerable improvement of technologic processes from point of view of their environmental impact, the heavy metal pollution could persist and can be spread through natural factors, such as wind, rain or water. Hence, even the isolated places, located

relatively far from initially infested areas, can be touched through different mechanisms of long-range transport of the polluting agents.

The natural muds represent special soil systems located in the areas relatively far from intense human activities. Due to their complex structure and to increased ion-exchange capacity, the muds are known for various therapy applications from the early times.¹⁻³ These systems could also give an image about the pollution with heavy metals. Included in lipophilic or in hydrophilic

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compounds, heavy metals can enter the human tissues, together with other compounds,⁴ reducing or even cancelling the therapy effectiveness.

The muds studied in this work are generally of a sapropelic type that means they correspond to the general definition of sapropelic muds as unconsolidated oozes consisting mainly of putrefied plant remains and found in anaerobic areas at the bottom of swamps, lakes, and shallow seas.⁵ Thus, the organic content of these muds is expectable to be relatively high.

The overall objective of this study was to determine chemical composition and structural features of various therapeutic muds in order to reveal the differences between them as well as to determine the content of heavy metals from natural or human activities. Based on the obtained results, a long term monitoring is intended for the sites representing a special interest.

RESULTS AND DISCUSSION

1. Thermal analysis

Generally, when the measurements were performed in presence of air, the thermograms of the studied muds presented significant exotherm processes which can be divided in two main regions (Fig. 1): one is oxidation, at relatively low

temperature (starting after 200 °C) and other is an exotherm decomposition (oxidative decomposition) which presented a maximum at ca. 470 °C for all samples.

In some cases, the oxidation and decomposition peaks are partly overlapped, in other cases there is a possible decomposition endotherm process between the mentioned exotherm processes. Some differences observed between the analyzed samples concerning the parameters of the oxidation and decomposition processes will be discussed below.

In the case of nitrogen atmosphere, only slight exotherm processes were observed, but endotherm decomposition processes of organic component were observed at temperatures higher than 300 °C. Considerably less intense exothermic decomposition processes were observed at temperatures higher than 450 °C (see Fig. 1).

It was also observed that all solid residues from DSC measurements in air presented various beige-orange colors due to considerable amounts of Fe (see below the results of elemental analysis), while in inert atmosphere, black residues were obtained due to partial carbonization of the organic material. Such behavior suggests the occurrence of low oxygen content in the organic components, possibly due to anaerobic decomposition of the vegetal remains in sapropelic muds.⁵

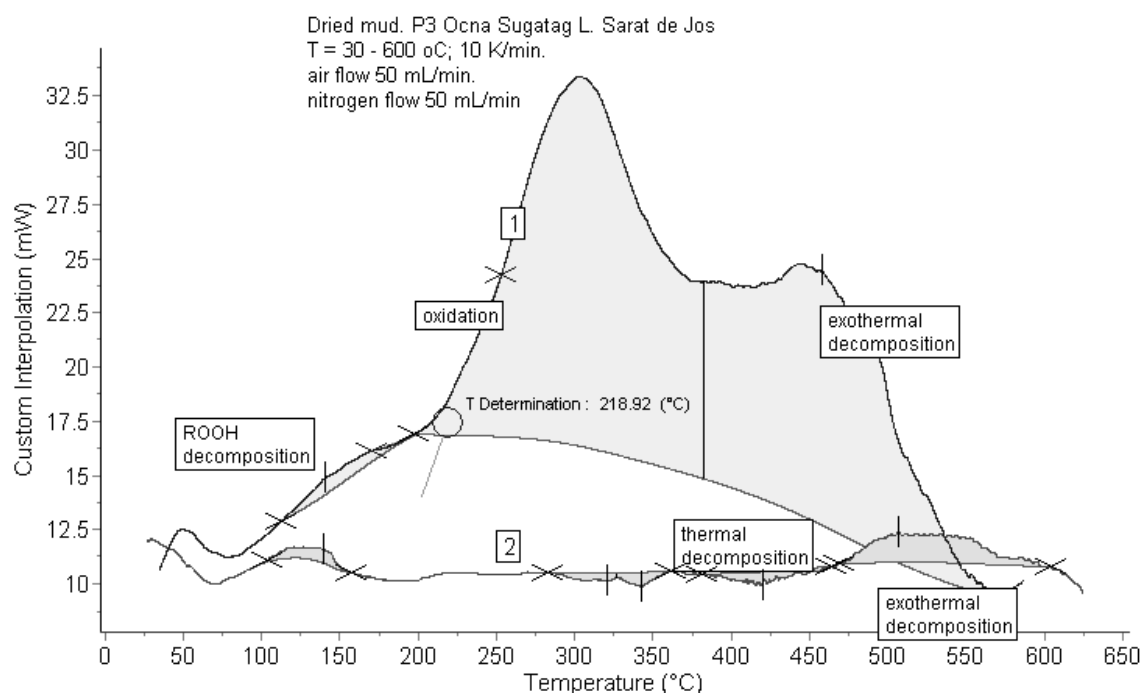


Fig. 1 – DSC curves of dried muds from Ocna Sugatag (L. Sarat de Jos, sample P3) in air (1) or in nitrogen atmosphere (2). Heating rate: 10 K/min.

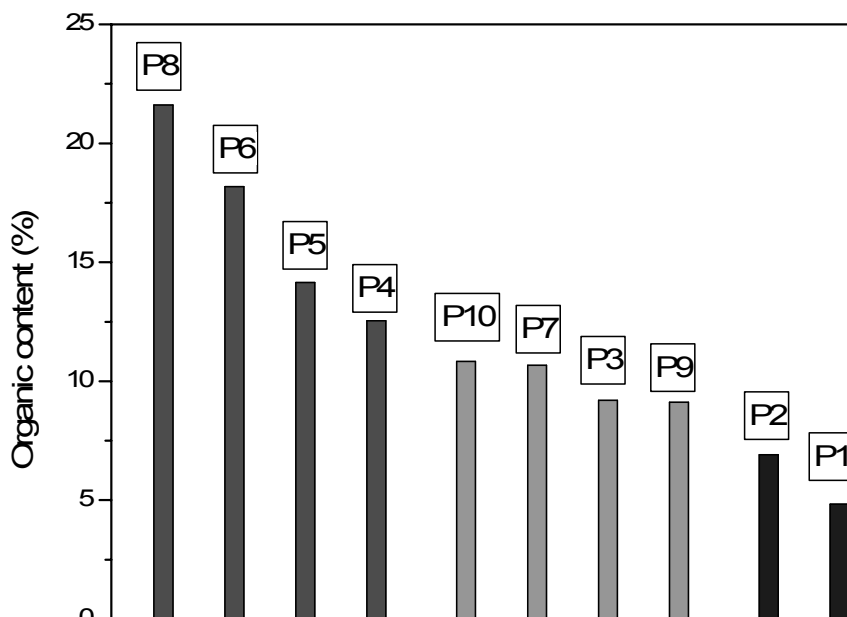


Fig. 2 – Ranking of the mud samples as a function of their organic content.

The results of thermal analysis confirmed the occurrence of a significant organic part in the case of the studied mud samples as shown in Fig. 2. The organic content appears to be different depending on the site, hence the studied muds can be gathered in three groups (Fig. 2): one contains more than 12 % of organic compounds, other contains 7-12 % of organic compounds and the third is lower than 7 %.

It is not clear if a correlation between the organic content and the therapeutic efficiency of the muds exists, but it could be observed anyway that the muds generally recognized to present high efficiency, such as P6 and P5, present also high organic content.

Though the structures of the DSC curves in air are rather similar, some significant differences in intensity of the thermal effects, as well as the kinetic parameters of both oxidation and decomposition, were observed (see Fig. 3 and Table 1). It can be clearly seen that the oxidation of the organic matter is more intense in the case of the samples P6 and P7, and the shape of the oxidation curve is similar for these samples. Other samples, such as P1, P3 and P4 presented quite different curves with lower thermal effects (see Fig. 3) and even slightly different shape of the DSC curves, with two well resolved exotherm peaks corresponding to lower temperature oxidation process and to oxidative decomposition, respectively. These different behaviors can be assigned to possible different interactions between the mineral matrix and the organic component: the occurrence of organic-inorganic nanostructures is

possible for these materials leading to increased thermal stability and hence to lower thermal effects and higher values of the parameters of thermal stability (see Table 1). Thus, even in the case of higher organic content, the thermal effect of oxidation as well as the total thermal effect of exotherm processes is lower in some cases, as for example for sample P8. A parameter X can be defined as shown in equation (1):

$$X = -C \cdot \Delta H_{exo} \quad (1)$$

where C is the organic content (see Table 1) and ΔH_{exo} is the sum of the thermal effects of oxidation and decomposition (the exotherm processes).

Such a parameter describing the “exothermicity” of a material could provide information about the stability of the organic-inorganic composite as well as about the energy content of such a composite. It is interesting to observe that the sample P6 presents the higher X value, while others can be gathered in two groups, one with X values between 40 and 100 and other lower than 40, as shown in Fig. 4. If compared with Fig. 2, this ranking is only partly the same, some other samples (such as P8), even containing more organic substance has a lower X value. Although at this time cannot be established a correlation between this parameter and the therapeutic efficiency of the studied muds, it is possible that high values of X parameter correspond to a high efficiency in the treatment of specific diseases.

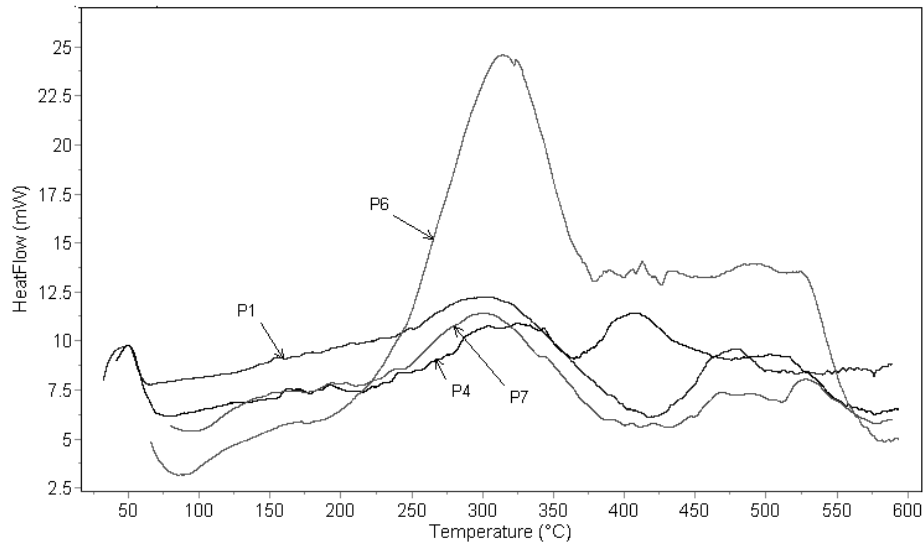


Fig. 3 – Comparative DSC curves of different muds.

Table 1

Results of thermal analysis characterization of mud samples

Sample	OOT (°C)	T _{max} (°C)	ΔH _{ox} (J/g)	T _{max} (°C)	ΔH _{ox} (J/g)	ΔH _{exo} (J/g)
P1	203.3	306.8	-227	477.3	-41	-268
P2	218.1	299.5	-234	469.6	-62	-296
P3	218.9	303.9	-517	457.7	-400	-317
P4	221.8	323.7	-180	408.3	-247	-427
P5	234.3	326.1	-410	488.9	-55	-465
P6	237.4	314.4	-505	524.5*	-240	-745
P7	225.7	304.8	-152	527.9	-152	-207
P8	218.4	297.8	-140	475.0	-48	-188
P9	218.3	299.0	-234	474.9	-16	-250
P10	213.8	285.6	-104	475.8	-7	-111

*flat domain with a small peak at 489 °C

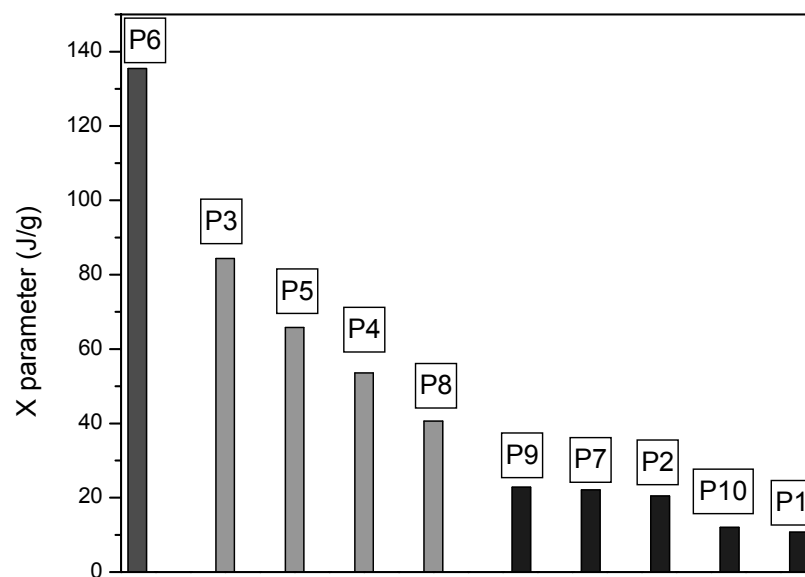


Fig. 4 – Ranking of mud samples based on the values of X parameter.

The oxidation onset temperature (OOT) which is a measure of the stability to oxidation of the organic compounds⁶ reaches the highest values for the samples P6 and P5. Other high OOT values were observed for samples P7 and P4, while the lowest value is observed for sample P1. The antioxidant species can result from the anaerobic decomposition of vegetal or animal organisms. The possible presence of antioxidants could be also benefit for the quality and therapeutic effectiveness of the muds, and should be remarked once again that the samples P6, P5 and P4 are again among the samples presenting highest OOT values (see Fig. 2).

2. ATR-FTIR analysis

Generally, the ATR-FTIR spectra indicated the presence of the humic substances in the analyzed muds. The major component appears to be the humic acid as indicated the occurrence of absorption bands in the region of 3500 - 3000 cm^{-1} , assigned to free (3610 cm^{-1}) or hydrogen bonds associated -OH groups (3290 cm^{-1}) as well as to N-H groups (3500-3000 cm^{-1} and 1650-1550 cm^{-1}).⁷

In Fig. 5, the absorption C-H band at 2920 cm^{-1} is clearly visible for sample P6, a weaker band exists in the case of P4, while no absorption bands are observed with P1 and P7 samples, proving the occurrence of different structures of the humic substances.

The wide absorption band at ca. 1400 cm^{-1} (Fig. 6) is assigned to the presence of aromatic structures⁷ which result from anaerobic decomposition and subsequent carbonization. At higher wavenumbers, namely in the range 1700-1600 cm^{-1} , it was observed a weak and wide band which could be assigned to the absorptions of C=O groups in acid compounds, C=C groups in unsaturated compounds and C-N groups in amides. At lower wavenumbers, intense peaks related to the Si-O and Si-O-Al groups were observed.⁸

As it can be seen from the spectra presented in Figs. 5 and 6, the nature of the humic substances appears to be different. If the therapeutic efficiency is related, at least partly, to the composition of the organic matter, and it is expectable to be so, differences in the efficiency of the muds could originate in differences in chemical composition of the organic matter.

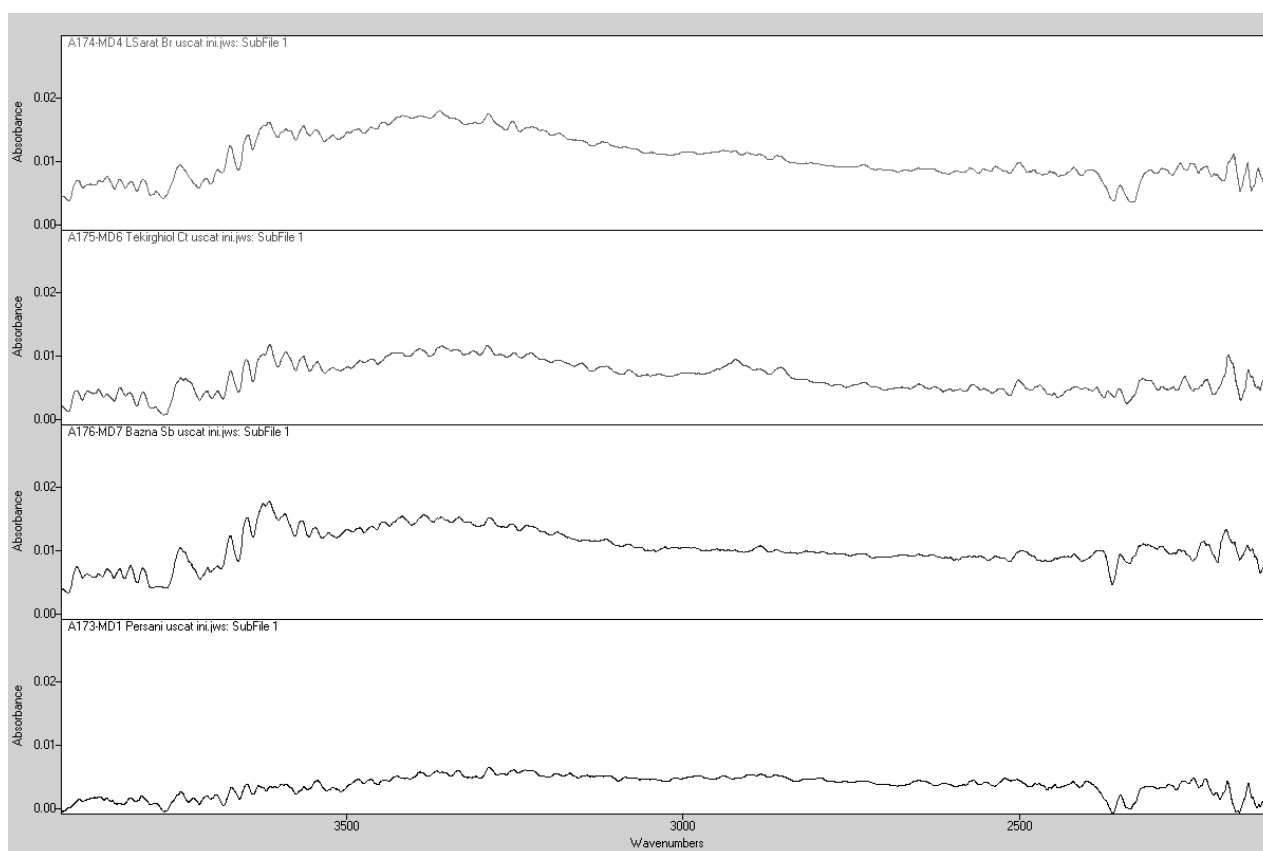


Fig. 5 – ATR-FTIR spectra in the region 4000-2000 cm^{-1} of some mud samples (in dried state): 1 – P4 (Lacul Sărat, Brăila); 2 – P6 (Tekirghiol, Constanța); 3 – P7 (Bazna, Sibiu); 4 – P1 (Perșani, Brașov).

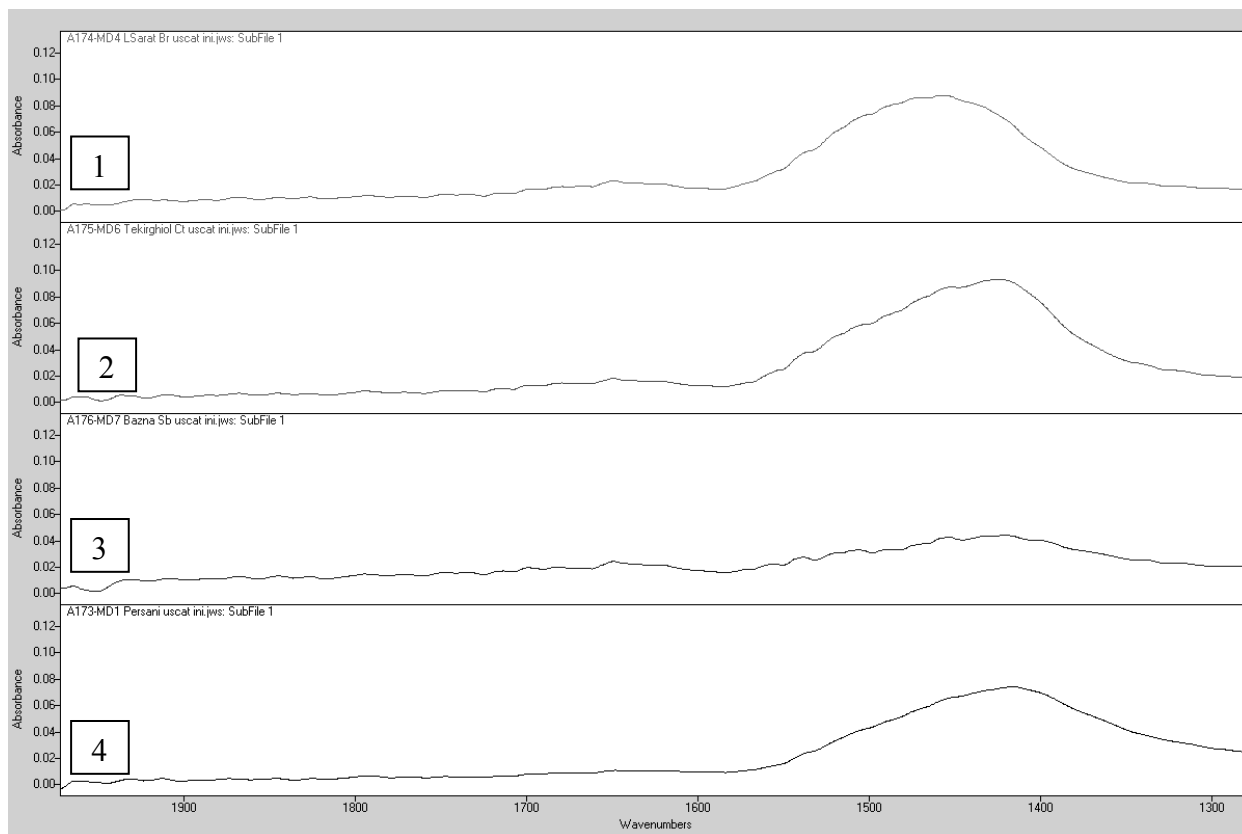


Fig. 6 – ATR-FTIR spectra in the region 2000-1200 cm^{-1} of some mud samples (in dried state):
1 – P4 (Lacul Sărat, Brăila); 2 – P6 (Tekirghiol, Constanța); 3 – P7 (Bazna, Sibiu); 4 – P1 (Perșani, Brașov).

3. Elemental analysis

EDXRF analysis

The elements detectable by EDXRF represent roughly 50 % of the sample mass of the analyzed muds. Among these elements (see Table 2), were found important amounts of Si, Al, Ca, and Fe which form the “mineral matrix” of the mud.⁹ The presence of other elements, such as K or Ti, was also observed in some cases. Silicon was the

dominant element in all studied samples, with except the sample P1 which contained a large amount of calcium.

The Fe content was roughly constant irrespective the site, but the content of other elements varied considerably (Table 2), suggesting a different composition of the mineral matrices. (The results concerning the structural characterization of mineral matrix of the studied muds will be presented in another paper.)

Table 2

Results of EDXRF elemental analysis of the studied mud samples

Sample no.	Concentration (%)						Total (%)
	Si	Fe	Al	Ca	K	Ti	
P1	18.4	4.8	1.9	37.2	-	-	62.3
P2	25.9	5.4	7.0	3.4	1.5	1.0	44.2
P3	18.7	5.9	5.1	2.0	0.8	1.5	34.0
P4	28.5	5.6	5.7	5.5	-	0.8	46.1
P5	33.8	5.5	5.5	8.4	0.9	1.2	55.3
P6	18.6	5.1	5.2	9.9	-	0.8	39.6
P7	25.9	5.5	8.4	4.4	0.8	0.9	45.9
P8	22.1	5.3	7.4	1.1	-	0.7	36.6
P9	26.1	5.3	8.5	-	0.9	-	40.8
P10	24.5	4.5	8.9	-	1.0	-	38.9

Samples P1 and P5 presented a higher mineral content. For the sample P1 was observed, as already mentioned, a higher calcium content possibly due to erosion of adjacent limestone rocks. P5 presented higher content of both silicon and calcium suggesting the presence of dispersive soils formed by silicates and carbonates. The samples P3, P8 and P9 presented lower content of Ca, indicating a clayey structure.

Beside the elements presented in Table 2, the presence of significant amounts of sodium in soluble salts was suggested by visual inspection of the samples after drying, when the formation of large white deposits was observed (Fig. 7). These elements as well as others, including halogens and heavy metals, were determined by instrumental neutron activation analysis (INAA), the results are summarized in Tables 3, 4 and 5.

Table 3

Results of INAA elemental analysis of some alkaline, alkaline earth metals and halogens in the studied mud samples

Sample	Concentration (mg/kg)							
	Na	Mg	Rb	Cs	Sr	Cl	Br	I
P1	9790	3320	22.5	2.26	1870	6150	11.6	18.5
P2	91500	7760	95.1	8.01	106	135000	9.56	<6.99
P3	75600	6530	55.9	3.32	139	93300	15.5	<7.5
P4	63800	15800	65.9	3.68	606	49400	69.2	15.4
P5	11300	8060	52.2	2.66	570	1570	20.4	21.1
P6	23600	16700	61.8	3.53	690	33700	101	93.1
P7	31100	12500	117	7.84	795	37700	129	144
P8	124000	11000	60.8	5.0	91.3	204000	8.93	<8.16
P9	59400	11700	107	8.9	116	86700	9.65	<10.6
P10	87500	11300	111	7.62	160	127000	7.69	<8.21

Table 4

Results of elemental analysis of some heavy metals by INAA on the mud samples (the Fe content was determined by EDXRF)

Sample	Concentration (mg/kg)							
	Cr	Mn	Ni	Co	Zn	Zr	Cd	Sr
P1	20.2	578	2.8	2.11	20.7	128	<1.8	1870
P2	91.5	563	40.9	12.1	159	138	<3.5	106
P3	77.2	391	29.8	9.74	206	306	<3.7	139
P4	66.7	673	37.5	10.3	90.8	147	<4.1	606
P5	62.6	637	27	8.63	50	289	<2.5	570
P6	73	514	35	9.43	158	123	<4.4	690
P7	104	698	53.5	14.7	136	139	<4.8	795
P8	68.5	409	29.7	13.4	100	89.6	<3.1	91
P9	85.8	537	49.2	13.3	192	136	2.3	116
P10	88.2	583	47.3	12.1	97.6	132	<3.2	160

Table 5

Results of elemental analysis of different metals by INAA on the mud samples (the Fe content was determined by EDXRF)

Sample	Concentration (mg/kg)								
	As	Sb	Ta	La	Ce	Au	Ag	Th	U
P1	1.42	0.19	0.36	13.2	23.5	0.02	<0.26	3.6	0.9
P2	14	1.31	0.83	29.5	56.5	0.02	<0.51	9.3	2.2
P3	7.66	1.85	1.1	31.7	66	0.03	<0.50	10.1	3
P4	5.76	0.674	0.66	22.9	47.4	0.01	<0.44	7.1	2.8
P5	3.68	0.462	0.75	25.3	51.9	0.01	<0.41	7.4	2.6
P6	5.47	0.653	0.64	25.3	48.8	0.01	<0.43	7.2	5.8
P7	8.08	0.934	0.91	32.7	66.8	0.003	<0.51	10.3	2.1
P8	6.25	0.618	0.62	20.1	41.7	0.01	<0.41	6.3	1.5
P9	13.5	1.46	0.85	32.4	57.7	0.03	0.56	9.6	2.3
P10	9.22	0.717	0.85	28.8	56.4	0.03	<0.49	9.3	1.9

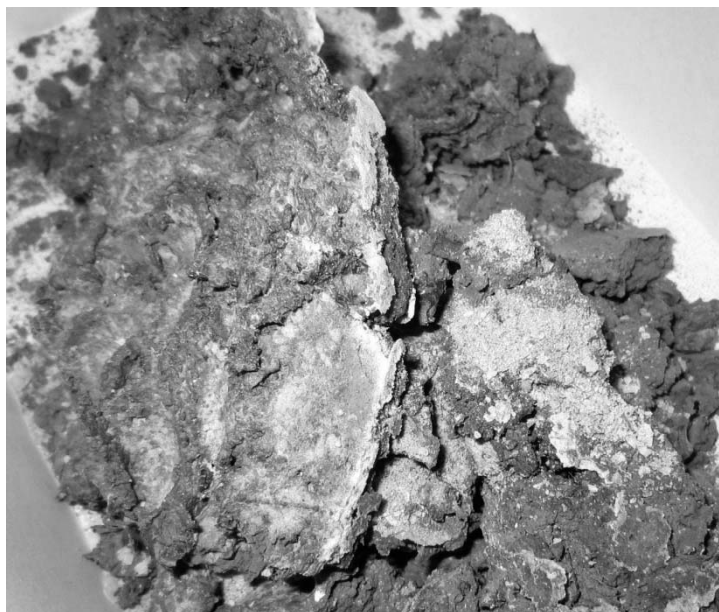


Fig. 7 – Dried P3 mud sample. Salt deposits are visible after oven-drying treatment.

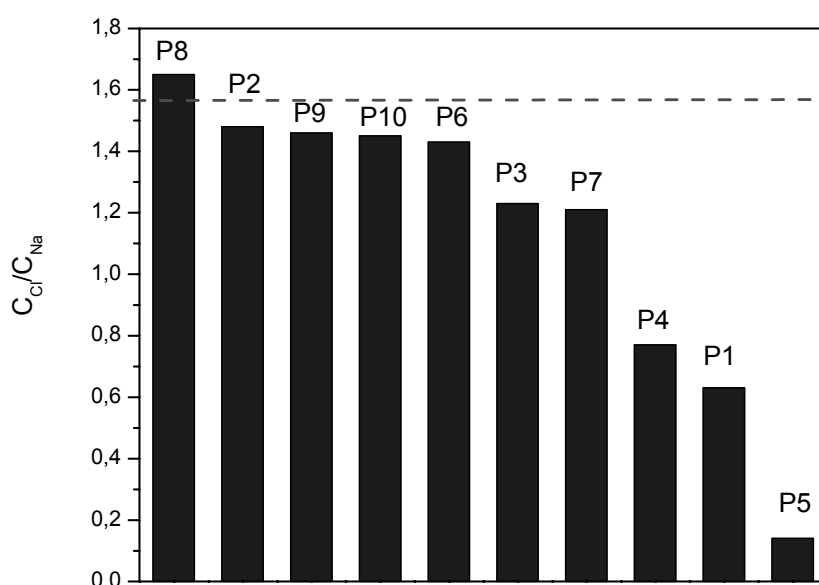


Fig. 8 – Ratios C_{Cl}/C_{Na} for the studied mud samples. The red line corresponds to the specific value of this ratio for sodium chloride (1.54).

Data in Table 3 indicate high concentrations of Na and Cl in concordance to the formation of white deposits observed upon the drying process. It should be noted that the ratio of the concentration of chlorine and sodium ions (C_{Cl}/C_{Na} , where C is the ion concentration in mg/kg in the analyzed sample) is different from one sample to another and is more or less different from the value of 1.54 (Fig. 8), specific for sodium chloride, indicating the presence of other sodium salts along with NaCl. When the ratio is lower than 1.54, either the presence of other anions (e.g. sulfate, carbonate) in considerable amounts, or the inclusion of sodium

ions in the mineral matrix is possible. When the mentioned ratio is higher than 1.54, there is an excess of chloride ions, hence the occurrence of different chloride salts (with magnesium or calcium) is possible.

Other elements in Table 3 are in normal limits for mineral waters and adjacent soils, even their concentrations are considerably higher than in ordinary conditions. Increased amounts of bromine, exceeding the warning threshold for less sensible applications of soil (*i.e.* 100 mg/kg),¹⁰ were observed for samples P6 and P7. The same samples presented also high iodine concentration

values. The strontium content is the highest in the sample P1, which also presented an exceptionally high concentration of Ca (see Table 2).

Generally, it can be said that the heavy metals concentrations (see Table 4) are normal or lower than the warning limits, even there are significant differences depending on the mud sample. An exception is the Cr content of the sample P7, which slightly exceeds the warning limit for sensible soil applications (*i.e.* 100 mg/kg of total Cr).¹⁰ Another exception concerns the cadmium content: all samples (excepting P1) presented higher values than normal threshold (1 mg/kg),¹⁰ and even higher than the warning limit for sensitive soil applications, *i.e.* 2 mg/kg.¹⁰ For the moment, it is not clear the source of this relatively high Cd content found in the studied samples.

The Zn concentration in samples P2, P3, P6, P7, P8 and P9 exceed the limits accepted for normal concentration of this metal in soil (100 mg/kg), but all these values are below the warning limit for soil sensible applications (300 mg/kg).¹⁰ The highest concentration was observed for the sample P3, taken out from Ocna Şugatag, namely 206 mg/kg. As the levels for other heavy metals remain in normal limits, it can be assumed that the increased levels of Zn concentration are related to the naturally occurrence of this element, rather to pollution as a result of human activities. According to Beyer,¹¹ the Zn concentration levels in the range of 90-200 mg/kg are typical for moderately polluted sediments.

The zirconium content is near to the average value mentioned for the surficial materials.¹¹ The highest value is observed again for the sample P3, but for the other samples presenting enhanced levels of Zn concentration, the Zr concentration is rather low, suggesting a natural occurrence of these metals.

The Ni concentration is lower than the normal limit (*i.e.* 20 mg/kg)¹⁰ only in the case of P1 sample. For the samples P2, P4, P6, P7, P9 and P10, the concentration of Ni is around twice the normal, but below the warning limit for sensitive

soil applications (*i.e.* 75 mg/kg). However, no correlation to the geographic position or to the relief form of the location can be established. The relative constant levels of Ni and Co could be related to the important presence of Fe (several percents) rather to the past influence of industrial activities that existed everywhere or to the actual intense vehicle circulation in the respective regions.

The concentrations of other elements found in the analyzed samples are included in Table 5. Among these elements, arsenic is present in quite high concentration, exceeding the normal limits (*i.e.* 5 mg/kg),¹⁰ but below the warning limit for sensitive soil applications (*i.e.* 15 mg/kg),¹⁰ in all cases, except the samples P1 and P5 which have low As content, within the normal limits. The samples P4 and P6 presented also low As concentrations, very close to the limit for normal soils. The As-enrichment of other muds, as for example P9 which slightly exceeds the mentioned limit for sensitive soil applications, can be related to the specificity of the mountain geothermal sites, where ancient volcanoes activity and subsequent transport processes may result in increased As concentration in the surface soils and waters.^{7, 12, 13} The concentrations found for Sb were below the normal limit (*i.e.* 5 mg/kg)¹⁰ for all samples.

EXPERIMENTAL

1. Materials

The mud samples collected and studied in this work are listed in Table 6 together their geographic coordinates and some general data concerning their appearance, behavior under drying and composition of the top water layer. All sampling operations, as well as sample conditioning were performed using non-metalli devices.

The mud samples were previously dried at 120 °C in oven in the presence of air for 5 hours, then, were grinded and sieved through a plastic device in order to separate both the coarse (non-friable) particles and the vegetal remains (Fig. 9). These fractions were subsequently separated using a tweezers and a magnifier. Only the fine fraction that represented at least 95 % of the dried sample weight was used for analysis.

Table 6

Mud samples studied in this work

Sample	Locality (County)	Geographic position	Remarks	General features of the mineral water top layer ¹⁷
P1	Perşani (Braşov)	N 45.78138; E 25.21114	Initial: black-brown color, rocks and frequent vegetal remains. Slight smell of humid soil. After drying, light-brown powder with some salt separation	Hypertonic sodium and calcium chloride and carbonate mineral waters ¹⁸

Table 6 (continued)

P2	Sovata Băi (Mureș)	N 46.498 E 24.76110	Initial: black color, vegetal remains. After drying: brown powder, salt separated	helyotherm lakes, sodium chloride mineral water (40 - 250 g/l) ¹⁷
P3	Ocna Sugatag - Lacul Sărat de Jos (Maramureș)	N 47.78333 E 23.93329	Initial: brown color, unctuous, homogeneous, bitter smell. After drying yellow-brown color, salt separated; vegetal remains	sodium chloride, 119 g/l ¹⁹
P4	Lacul Sărat (Brăila)	N 45.22880 E 27.64456	Initial: black, viscous material; intense smell of mercaptans or H ₂ S. After drying: black solid and white salt separated; no rocks or visible vegetal remains	salinity, 70 - 84 g/l; S, Cl, Br, Na and Mg containing compounds ¹⁷
P5	Amara (Ialomița)	N 44.61994 E 27.31992	Initial: brown color, viscous, apparently homogeneous, no smell or slight mercaptane smell inside. Vegetal remains present. After drying: solid, light brown colored, no salt deposits visible, frequent vegetal remains (slim stalks, fibrillar roots)	water springs containing Na, K bicarbonate, sulfurous and light sulfate compounds ¹⁷
P6	Techirghiol (Constanța)	N 44.05743 E 28.59599	Initial: black color, viscous, homogeneous, strong smell of mercaptans or H ₂ S. After drying: ochre-yellow solid, apparently homogeneous, without visible vegetal remains or salt separation	salinity, > 60 g/l, pH 8.3-8.4; Ca, Mg in chloride and sulfate compounds ²⁰
P7	Bazna (Sibiu)	N 46.20047 E 24.28046	Initial: brown-reddish, viscous, homogeneous, bitter smell. After drying: brown-olive material with some white deposits on the surface	mineral water containing Na chloride/iodide
P8	Băile Figa – Lacul Sărat (Bistrița-Năsăud)	N 47.18254 E 24.13623	Initial: brown-grayish color at surface (brown-dark gray inside), homogeneous, no visible rocks or vegetal remains, no smell. After drying: beige and dark gray spotted solid with important white deposits. Some rocks and few vegetal remains found during the sieving	sodium chloride thermal water ²¹
P9	Sovata Băi (Mureș) – bază tratament	N 46.5770 E 25.07801	Initial: light brown-orange in the superficial dried area, dark-gray inside, smell of wet soil. After drying: relative hard solid, difficult to crush, black-gray-beige spotted	helyotherm lakes, sodium chloride mineral water (40 - 250 g/l) ¹⁷
P10	Gherla (Cluj)	N 47.0196 E 29.90043	Initial: black, viscous, homogeneous material. After drying: dark brown solid with important white deposits	Na, K, Ca, Mg in chloride, bromide, sulfates and bicarbonates

2. Instruments and methods

2.1. Thermal analysis

A Setaram 131 Evo (Setaram Instrumentation, Caluire, France) instrument was used to perform the DSC measurements. The non-isothermal (ramp) measuring mode has been applied in this study, using either inert (nitrogen) or oxidative (air) atmosphere. The gas flow was 50 mL/min. and the heating rate was 10 K/min. in all cases. Dried mud samples, in the form of fine powders, were placed in alumina crucibles with pans, the sample mass being around 18 mg in each case.

The oxidation onset temperature OOT values as well as the other parameters characterizing the different processes (such as the oxidation or the decomposition), namely T_{\max} (the temperature in the maximum, of the peak) and ΔH (the

thermal effect of the process) were obtained from non-isothermal DSC measurements in air, using the procedures described in international standards for either organic compounds (hydrocarbons)¹⁴ or polymer materials.^{6, 15}

The organic content was assessed using the sample masses before and after the DSC measurements in the range 30-600 °C in presence of air, using the following formula:

$$C = \frac{m_o - m_f}{m_o} \cdot 100 \quad (2)$$

where C is the organic content in percents, m_o and m_f are the mud sample mass before and after the DSC measurement.

The loss of water or of other inorganic volatiles as well as the occurrence of physical processes in the inorganic matrix in this temperature range was however neglected at this stage.

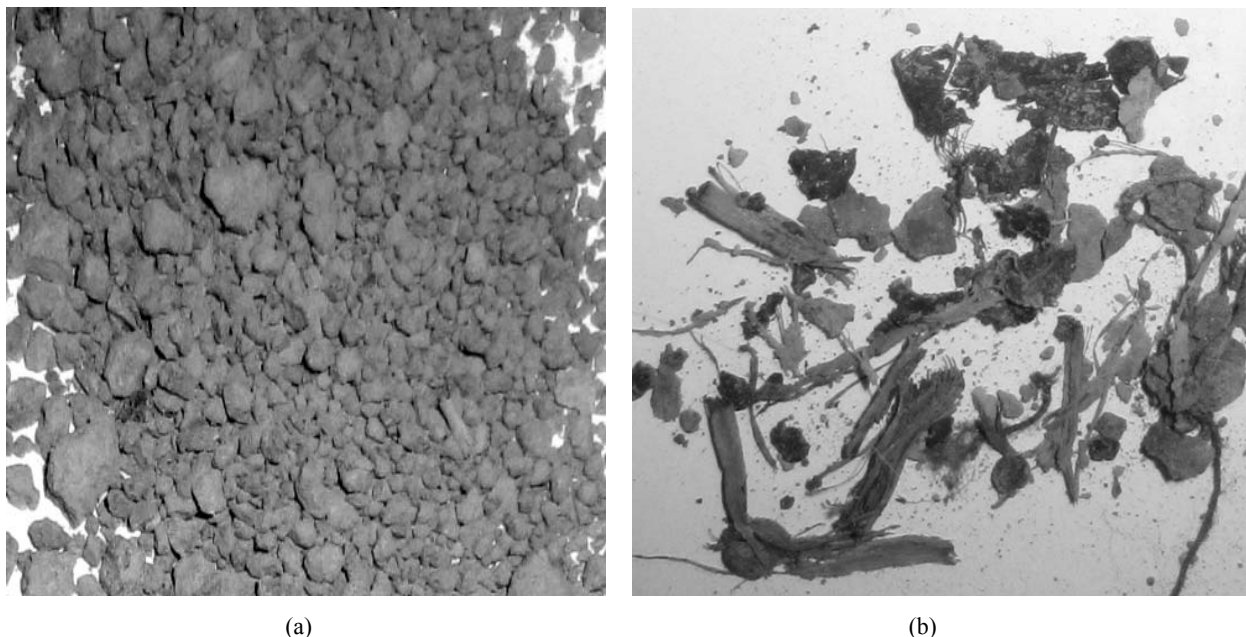


Fig. 9 – Fractions separated from the sample P9 after drying and sieving:
(a) coarse particle fraction; (b) vegetal remains.

2.2. Attenuated Total Reflectance – Fourier Transform Infrared spectroscopy (ATR-FTIR) spectroscopy

The ATR-FTIR spectra of the studied mud samples (in dried state) were recorded in the range 4000–400 cm^{-1} using an ATR module type ATR Jasco Pro 470-H coupled to FTIR-Jasco 4200 spectrometer, with diamond crystal. The resolution was 2 cm^{-1} and the number of scans was 48 for each spectrum. The processing of the spectral data was performed by specific Jasco Spectra Analysis software for establishing the peak positions and absorbance values. Both KnowItAll FTIR Jasco software and literature reference data were used for bands assignments.

2.3. Energy Dispersive X-Ray Fluorescence (EDXRF)

EDXRF analysis has been performed directly on dried mud samples, using a ElvaX Light XRF analyzer (Elvatech, Kiev, Ukraine) on samples of ca. 3.4 g. The irradiation time was 30 minutes. The calibration was made by Y standard solution added directly to mud matrix as well as by using different simpler compounds and their mixtures with known concentrations. Comparative XRF measurements on selected samples were also performed at the Laboratory of Mechel S.A. Târgoviște.

2.4. Instrumental Neutron Activation Analysis (INAA)

INAA was performed at the pulsed fast reactor IBR-2 of the Joint Institute for Nuclear Research (JINR), Dubna, Russia. To analyze as many as possible elements, both short term (60 s) and long term (63 h) irradiations were used. Short term activation was performed in the conventional irradiation channel while, in the case of long term irradiation, the Cd-screened irradiation channel was used.

To determine the elemental concentrations a comparator method was used employing IAEA standard reference materials 1633b (coal fly ash), 2709 (Trace elements in soil), 2710 (Montana Soil), 2711 (Montana Soil) and 433 (Marine sediment).

After short time irradiation, each sample was measured twice, after 2 and 10 minutes, for about 5 and 12 minutes, respectively.

In the case of long time irradiation, gamma ray spectra were recorded after 4 and 14 days cooling time. All gamma ray spectra were recorded and processed using both Genie 2000 software and proprietary software developed at the Frank laboratory for Neutron Physics of JINR.¹⁶ In this way, the final uncertainties as calculated by taking into account statistic counting, sample preparation and detector calibration varied between 3 % for Na, Al, Zn and As and 40 % for I. A total of 37 elements were determined.

CONCLUSIONS

A specific interaction between the organic component and the mineral matrix of the muds is suggested by the differences observed for both structure of DSC curves and kinetic parameters of oxidation and decomposition processes.

The nature of the organic matter appears to be different in ATR-FTIR spectra. The composition of the humic substances could induce specificity in the therapeutic efficiency through different properties, such as: the ion exchange capacity, hydrophylicity, antioxidant activity, etc.

The studied muds are generally rich in sodium being formed in the presence of salty water. Other elements are also present, but their concentrations are generally within the normal limits for the soils, even a certain increase in metal ions concentration (as for example for Zn) could be considered normal in the case of mineral waters present in

contact with the muds. Hence, no evidence of pollution effects as a result of human activities can be concluded at this stage. A high concentration of Cd was however observed for all samples, but there is no clear understanding of this result.

Increased concentrations of As found in some samples can be related to the specific natural conditions of geothermal areas.

Further investigations will allow establishing the structure of the mineral matrix of the muds, to better understand the significance of increased concentrations of some heavy metals as well as to analyze the chemical nature of the organic compounds present in the muds.

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