ORIGINAL PAPER

PHYSICO-CHEMICAL CHARACTERIZATION OF THERAPEUTIC MUDS FROM BRASOV COUNTY

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Abstract. *This article highlights the main physico - chemical characteristics of the therapeutic muds collected from localities mentioned by the literature (Rodbav, Homorod and Persani), but also from two other localities discovered during the study period, namely Rupea and Grid. The study and presentation of the sources of mass treatment was, however, a brief one over time, and empirical valorification was made by the locals. Therefore, the present paper aims to shows the particularities of the treatments in the Brasov County, presenting the way in which they have been exploited in the past. Through the information contained: the history of knowledge and valorisation of therapeutic muds and their physico-chemical characteristics, this work is considered to present a high interest in the matter of completing and updating the information about the treatments in Brasov County.*

Keywords: *therapeutic mud, sapropelic mud, SEM-EDS, ATR-FTIR.*

1. INTRODUCTION

In the guide of the Ministry of Health [1] and other scientific papers [2-4] it's mentioned that in Romania are three types of muds: sapropelic, mineral and peat mud. Since ancient times, Romania has been recognized for the balneological / therapeutical potential [5-8]. For Brasov County, the literature mentions the existence of mineral muds at Rodbav, Homorod and Venetia de Jos and the sapropelic muds at Persani [9]. In the formation of these mud types, the geological conditions specific to Brasov County and the existence of different sources of mineral waters such as the chlorosodic mineral springs in the Persani - Grid area, the chlorosodic, bicarbonate sulphurous springs in the area Rupea - Homorod and the mixed mineral water sources in the Rodbav area. These natural resources (mineral waters and therapeutic muds) have been harvested locally until 1989, with small resorts with a seasonal or permanent character. After 1989, the mentioned spa facilities were left in paragliding, the only location in the county where the mineral waters and the therapeutic sludge (rudimentary capitalization though), being Persani and Rodbav, the complex has been upgraded, but the natural therapeutic resources were not valorised.

The information presented in this paper may be useful to local communities about the therapeutic muds and providing data on the physico-chemical parameters of the mud samples.

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2. MATERIALS AND METHODS

In this article were used three categories of data: 1. information obtained after consultation of specialized scientific papers, including cartographic materials (i.e. geological map of Romania 1: 200000, Romania's topographic map 1: 25,000); 2. information obtained from investigations field during 2011-2016 (e.g. GPS surveys, sampling of muds); 3. analytical data obtained by physico-chemical analysis of mud samples.

On the territory of Brasov County (Fig. 1), according to the scientific literature, therapeutic muds are found at Persani, mineral muds are found at Homorod and Rodbav. Taking into account the characteristics of the Grid area near the Persani (forming conditions, physico-chemical peculiarities of the analyzed sludge sample), the authors believe that there is a sapropelic mud area, and also in Rupea (near Homorod) are favorable conditions for the formation of mineral muds with different peculiarities depending on the chemical parameters of mineral water sources [9]. The mud samples were collected in November 2016 from the most important locations of Brasov County (i.e. Persani, Grid, Rodbav, Rupea, and Homorod). From each site was collected one sample, except Homorod from which were collected two samples: a sample from the eruption site (with sulphurous mud) – named "Homorod 1" and a sample of the sulphurous mud collected from the accumulation site "Homorod 2".

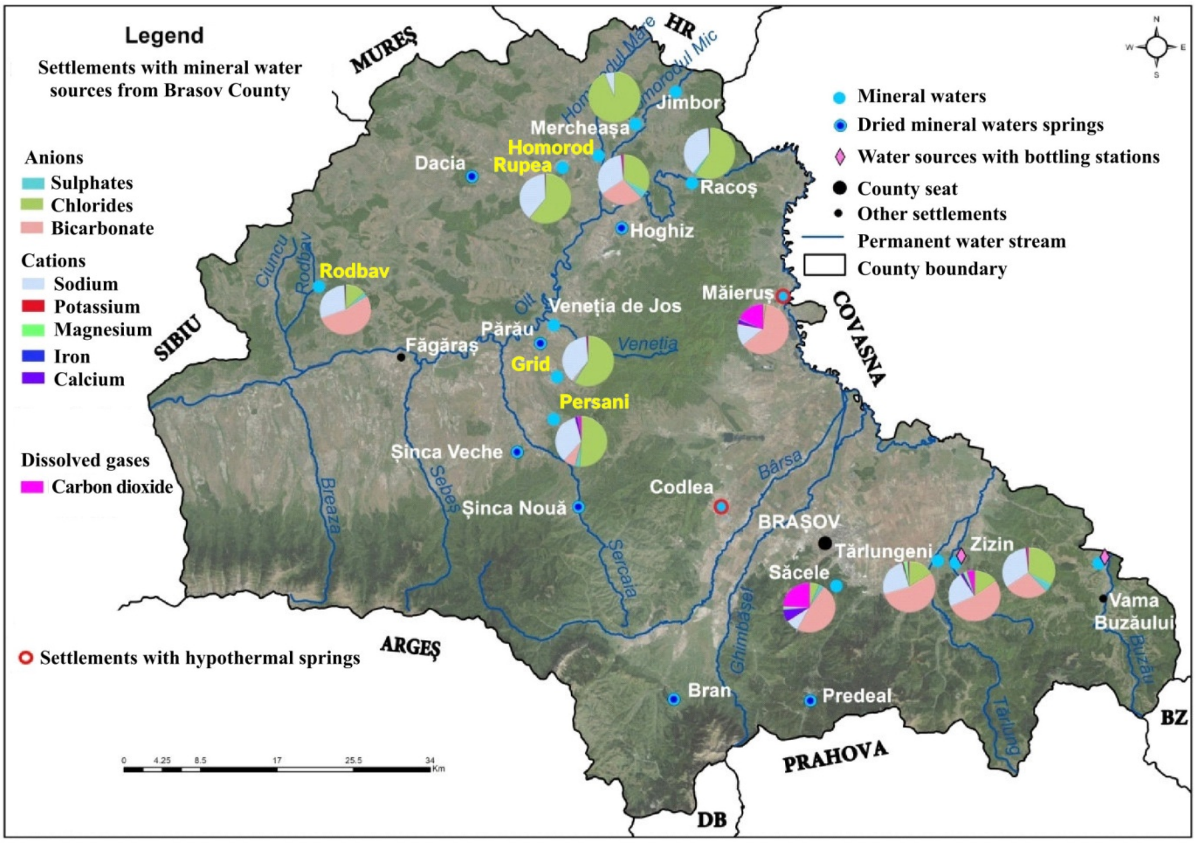


Figure 1. Mineral water sources in Brasov County. The mud samples were collected from: Persani, Grid, Rodbav, Rupea, and Homorod (marked on the map with yellow color).

The mud samples (about 500 g) were collected in polyethylene containers, carried using thermally insulated containers at 4 °C [6]. Half of each sample was dried in oven for at least 48 hours at 60 °C, passed through a 2 mm sieve, and homogenized, and the other half was stored in a freezer at -18 °C [10-12].

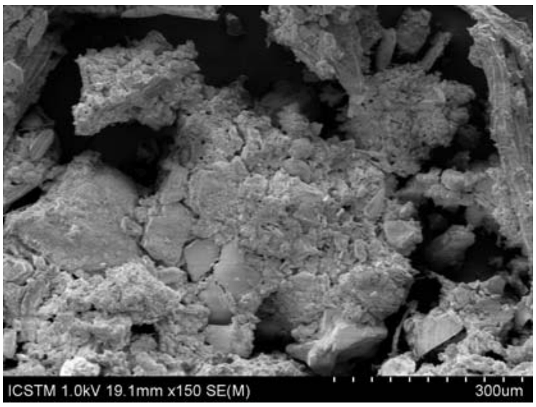
In order to perform qualitative and quantitative analyzes of the mud samples, the scanning electron microscope SU-70 (Hitachi) coupled with energy dispersive spectrometer UltraDry (Thermo Scientific) was used. The parameters used to obtain morphology images were: accelarating voltage (Vacc) 1 kV; working distance (WD) 18–19 mm; magnification range 150X–5000X, and in order to obtain the chemical composition (EDS) the parameters used were: Vacc = 15 kV; WD = 14–15 mm; magnification range: 500X–1000X. For SEM-EDS were used the dryed samples mounted on the stub directly on the double-adhesive carbon tape. The characterization of the samples was completed by Fourier transform infrared spectrometry (FTIR), using Vertex 80 (Bruker) spectrometer equipped with attenuated total reflection (ATR) device. The scanned spectral range was 4000 – 400 cm^{-1} and for each sample were run 32 reads, and the final results are expressed as the mean value. For ATR-FTIR were used both sample types (dry and wet) mounted directly on ATR support. This two techniques (i.e. SEM-EDS and FTIR) are widely used as complementary analysis methods in physico-chemical characterization of microplastics and polymers [13, 14], paper, wood, metal and lacquer [15-18], ceramic / painted pottery, paintings and rock-cut panels [19-24] etc.

3. RESULTS AND DISCUSSION

In the scientific literature [2, 4] are presented some information on the chemical composition of the therapeutic muds from Brasov County, but only for a few locations and also the data is summarized. For example, according to the Institute of Balneology [23] the muds from Homorod contains 568.506 ‰ of water, 30.823 ‰ of mineral substances and 400.671 ‰ of volatile mineral substances, and the muds from Rodbav has a mineralization of 1.124 ‰ and contains 0.01 % FeS.

The mud samples collected in November 2016 have been analyzed by SEM-EDS and the morphology images, EDS spectra and obtained results are presented in Figs. 2-7, as well as the elemental compositions (presented in Table 1).

The obtained SEM morphology images of the mud sample collected from Persani, indicate a granular structure with coarse inclusions (Fig. 2a) and presents other impurities, such as roots or different algae species (*Epithemia sp., Navicula sp.*, *Cymbella sp.*) (Fig. 2b). From the data obtained by EDS, a quite homogeneous chemical composition is observed, the elements being evenly distributed on the surface of the sample, with the exception of sodium, chloride, calcium and potassium, whose distribution is granular (Fig. 2d).



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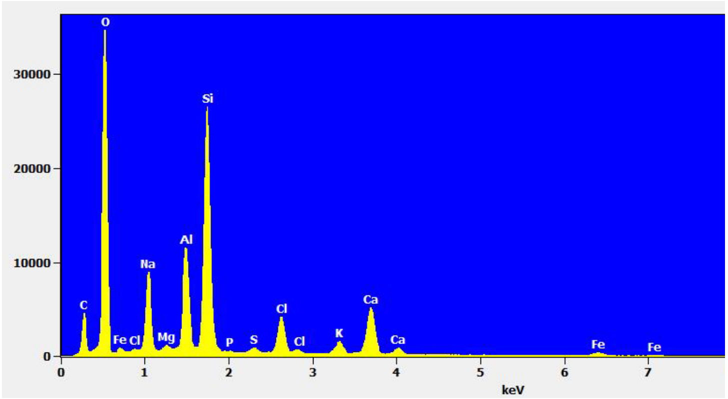

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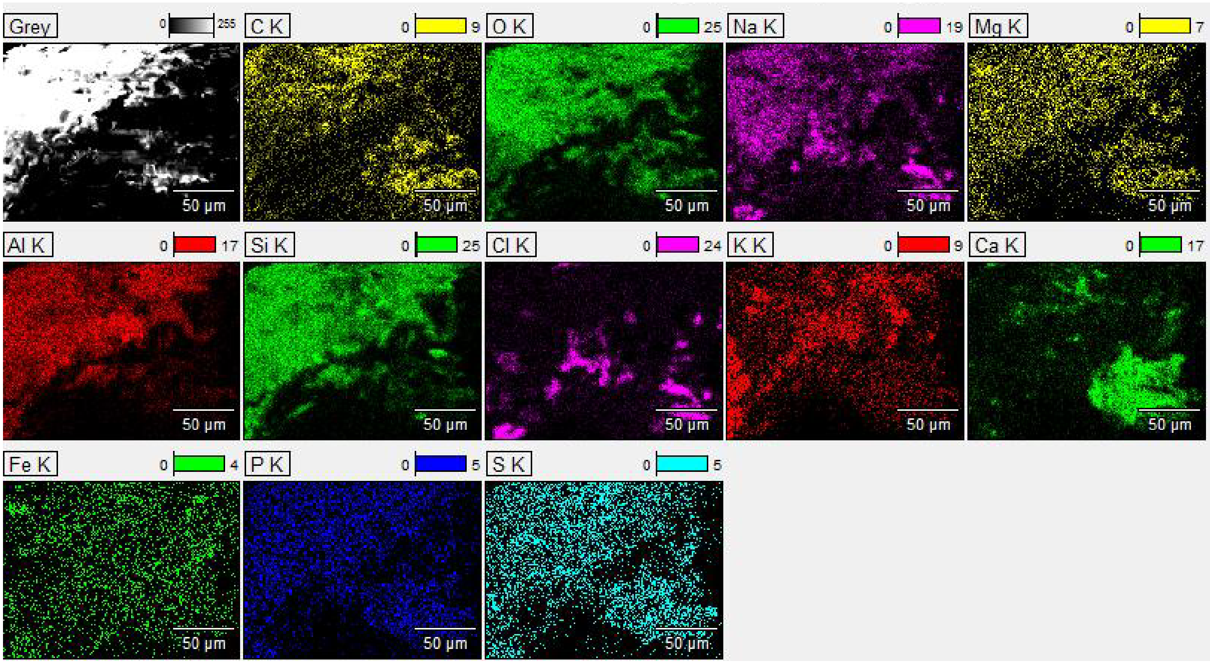

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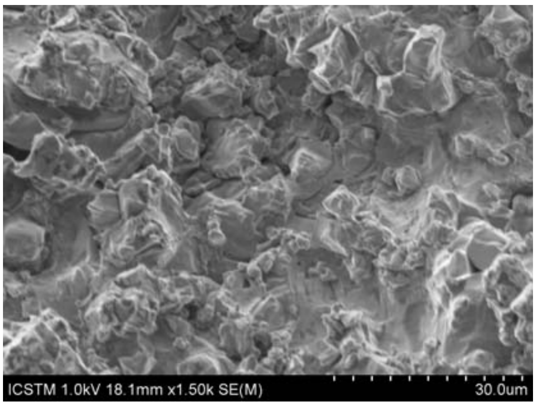
Figure. 2. Persani sample: a. Morphology image (general); b. *Navicula* sp. found on mud sample; c. EDS spectra; d. EDS elemental maps.

For Grid sample, SEM morphology images (Fig. 3a) indicate a granular sample structure without any other impurities (e.g. leaves, stones, roots, etc.), and from EDS data, it is observed that, from the point of view of the chemical composition, the sample is quite homogeneous, chemical elements being evenly distributed on the surface of the sample except for sodium and chloride (sodium chloride) which is having a granular structure (Fig. 3c).



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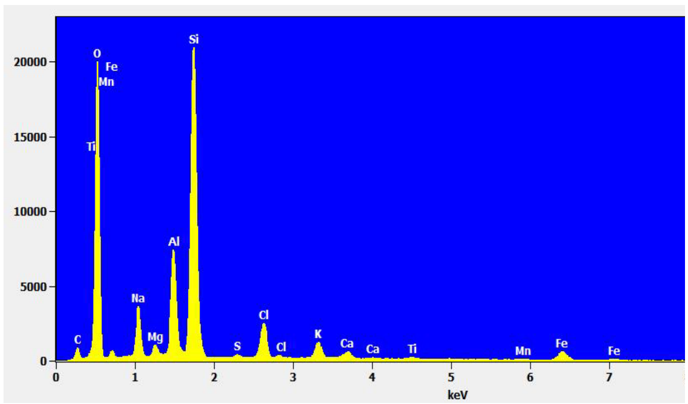

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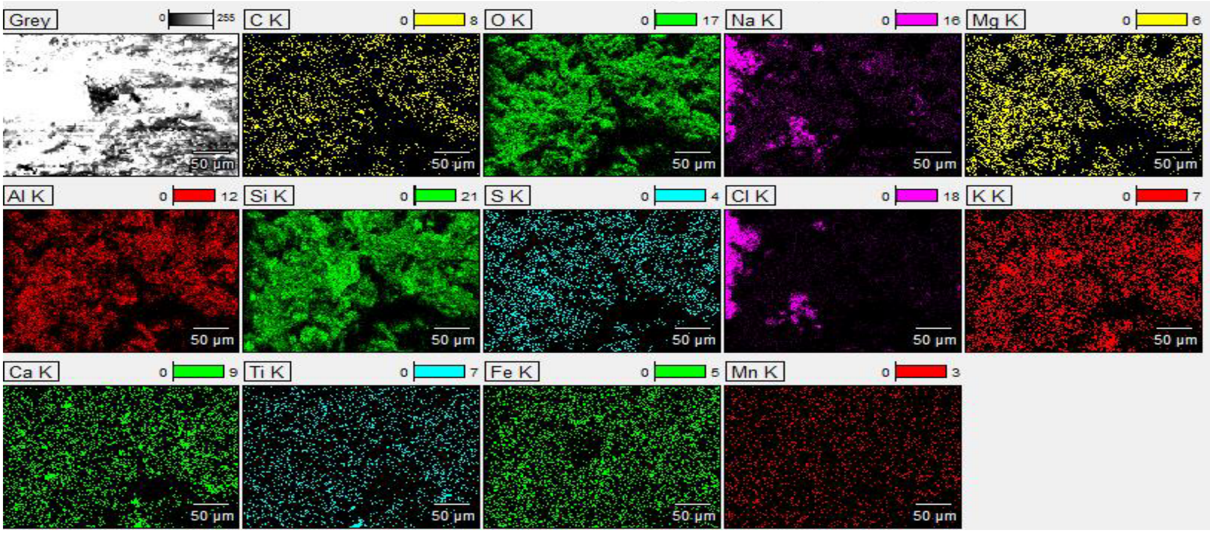

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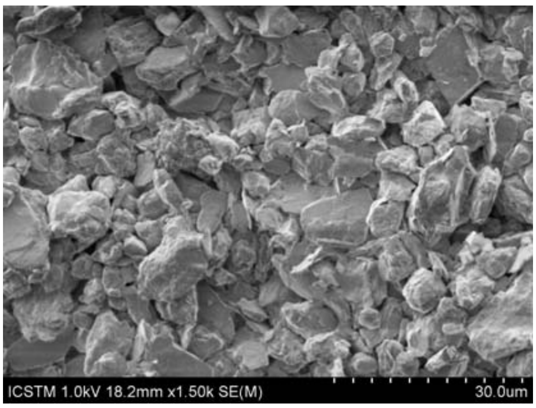
Figure. 3. Grid sample: a. Morphology image; b. EDS spectra; c. EDS elemental maps.

The SEM morphology images of Homorod 1 indicated that the sample has a granular structure and is compact without any other impurities (Fig. 4a) and from the point of view of the chemical composition, the data obtained by EDS showed that it is a fairly homogeneous sample, the chemical elements being evenly distributed, with the exception of granules and potassium, which have a granular distribution (Fig. 4c).



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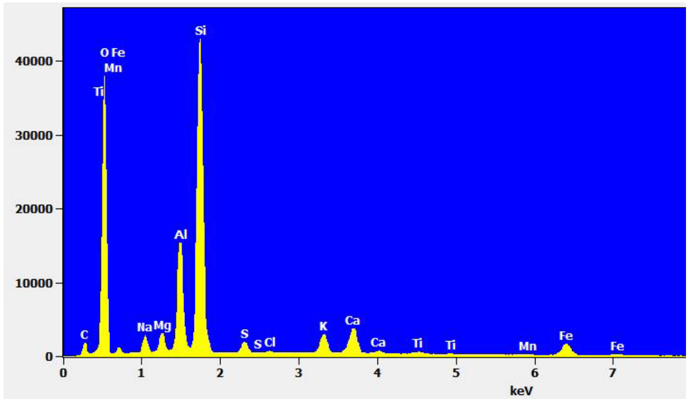

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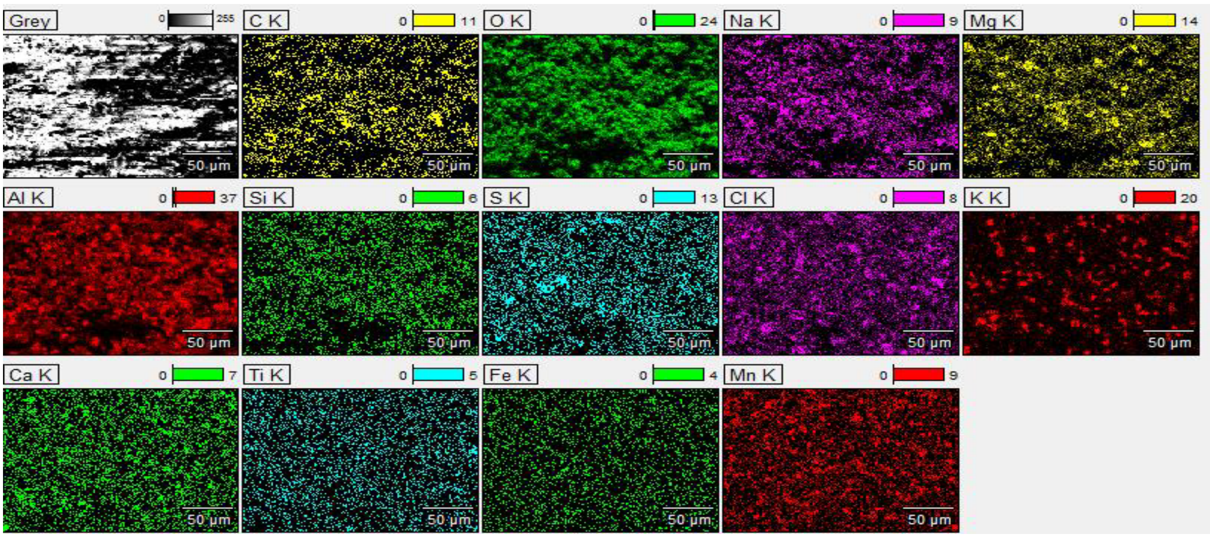
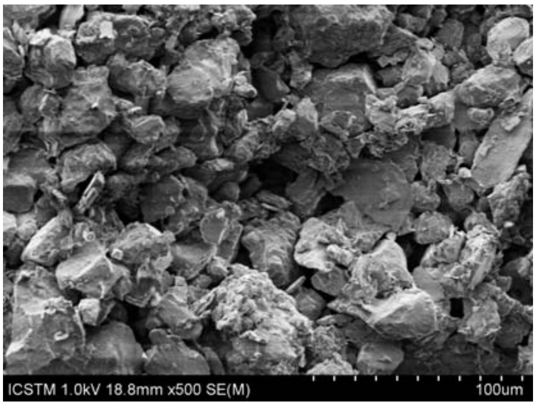


c.

Figure. 4. Homorod 1 sample: a. Morphology image; b. EDS spectra; c. EDS elemental maps.

The Homorod 2 sample has a compact, granular structure but with thick inclusions, and from a chemical point of view the sample is not homogeneous, the elements presenting a non-uniform distribution (Fig. 5), but similar to that of Homorod 1.



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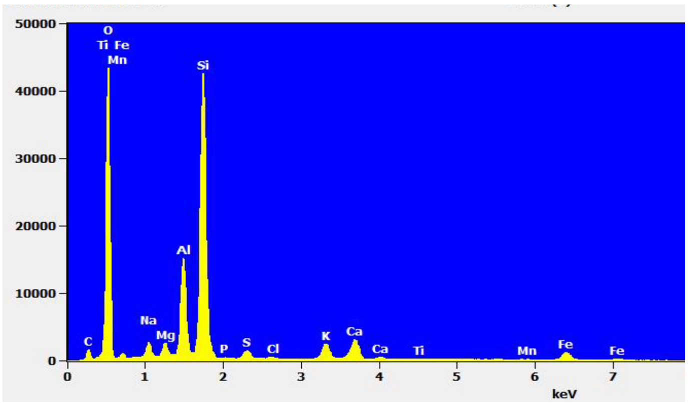

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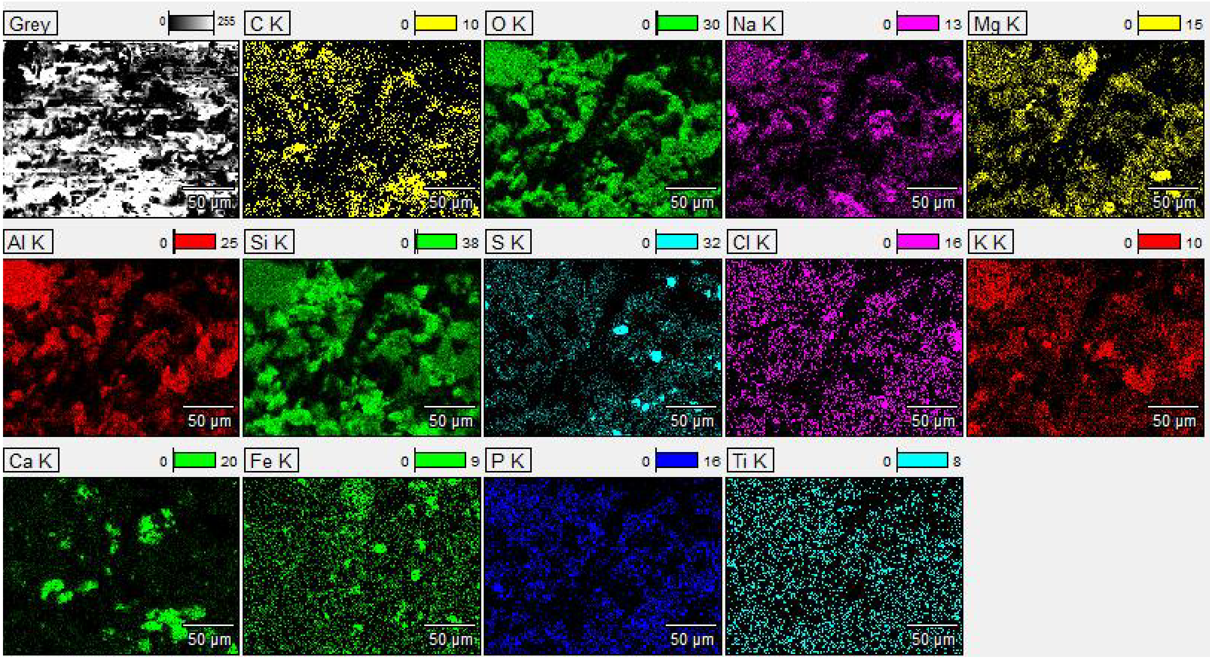

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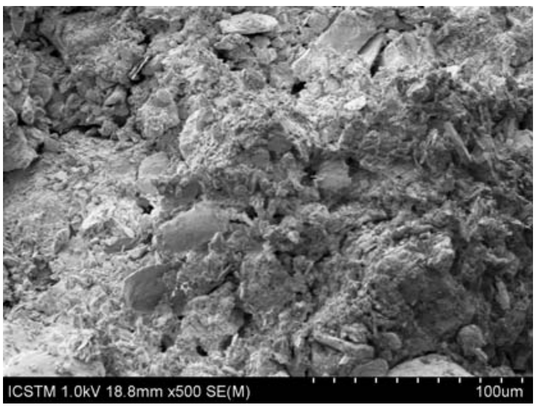
Figure. 5. Homorod 2 sample: a. Morphology image; b. EDS spectra; c. EDS elemental maps.



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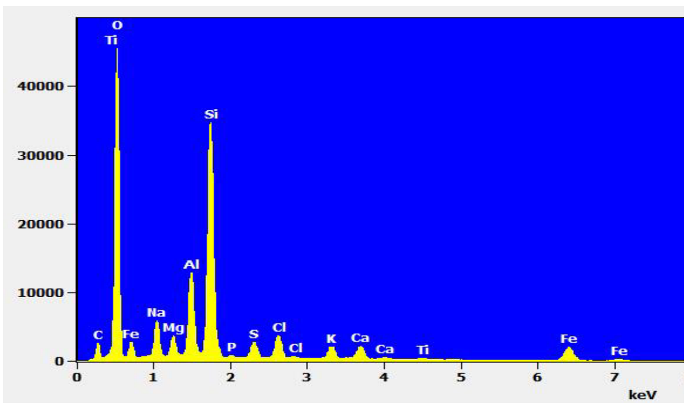

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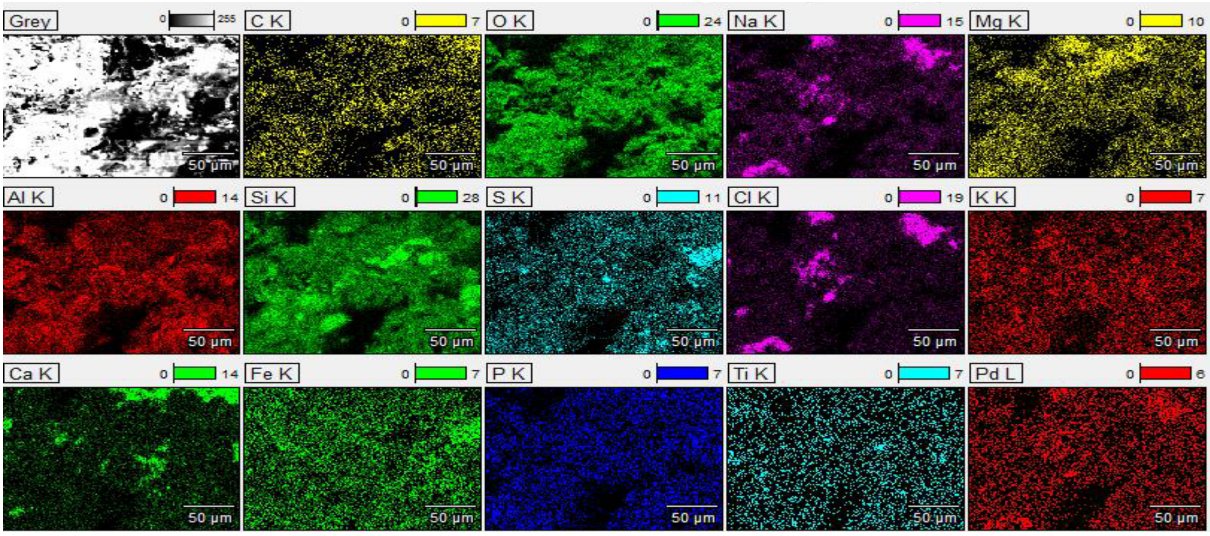
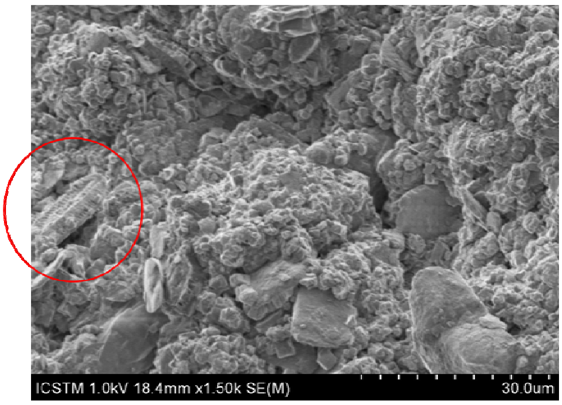


c.

Figure 6. Rodbav sample: a. Morphology image; b. EDS spectra; c. EDS elemental maps.

For the Rodbav sample, SEM morphology images showed that it is a compact sample with a granular structure containing coarse inclusions (Fig. 6a). EDS data show that from the point of view of the chemical composition, the sample is quite homogeneous, the chemical elements being evenly distributed on the surface of the sample, except for sodium, chlorine, silica and calcium, whose distribution is granular (Fig. 6c).



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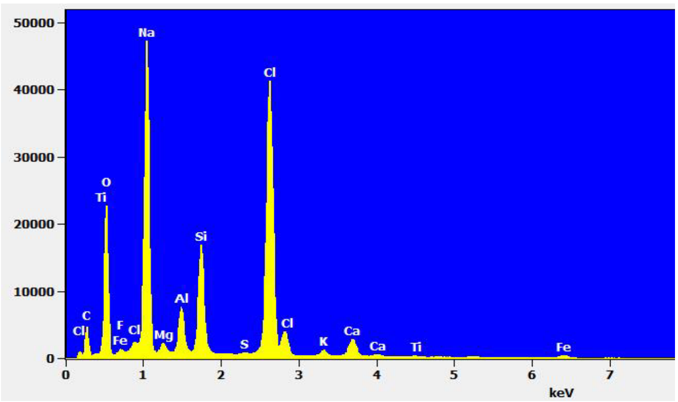

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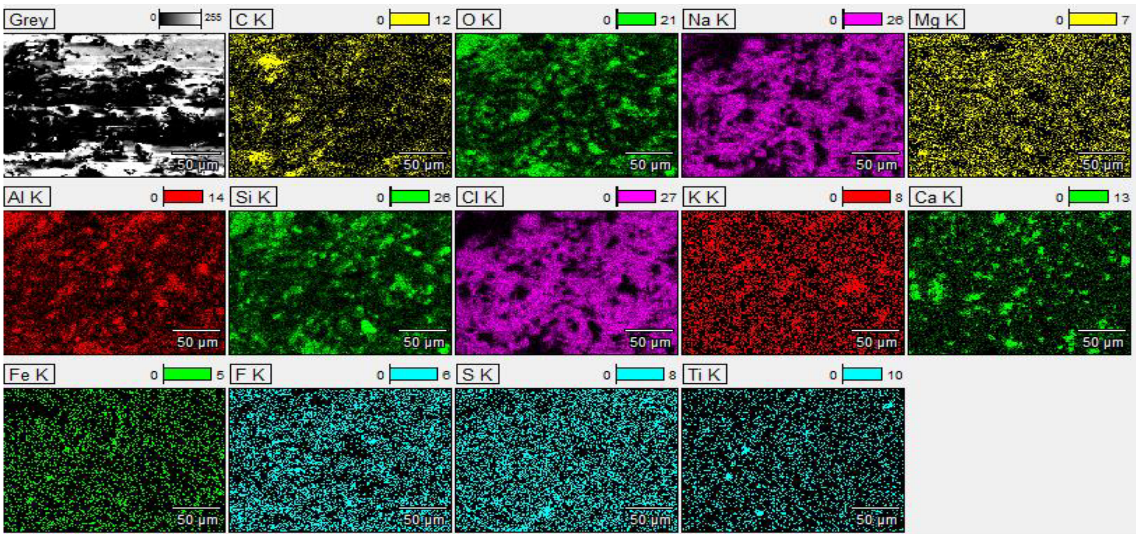

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Figure. 7. Rupea mud sample: a. Morphology image (red circle marks the *Navicula* sp. presence); b. EDS spectra; c. EDS elemental maps.

The SEM morphology images of the last mud sample (collected from Rupea) showed that the sample is compact, with a granular structure (Fig. 7a), with few impurities (*Navicula* sp. algae) (Fig. 7a – red circle), and from the point of view of the chemical composition, according to the data obtained by EDS, the sample is quite homogeneous, the elements being evenly distributed on the surface of the sample, with the exception of aluminum, silica and calcium, whose distribution is granular (Fig. 7c).

Table 1. Elemental composition (expressed as wt. % ± % error) of mud samples obtained by SEM-EDS.

Element	Samples					
[wt. % ± % error]	Persani	Grid	Homorod 1	Homorod 2	Rodbav	Rupea
C	12.39 ± 0.11	5.91 ± 0.11	5.56 ± 0.08	5.39 ± 0.08	7.70 ± 0.12	14.49 ± 0.17
O	50.13 ± 0.26	47.81 ± 0.26	47. 75 ± 0.24	51.71 ± 0.26	49.37 ± 0.25	29.66 ± 0.18
Na	5.69 ± 0.04	4.51 ± 0.05	1.59 ± 0.02	1.52 ± 0.02	3.42 ± 0.03	0.41 ±0.06
Mg	0.27 ± 0.02	0.73 ± 0.03	1.21 ± 0.02	1.01 ± 0.02	1.49 ± 0.03	19.24 ± 0.08
Al	5.32 ± 0.04	6.45 ±0.06	6.81 ± 0.04	6.71 ± 0.04	5.48 ± 0.04	0.41 ± 0.02
Si	14.05 ± 0.06	21.53 ± 0.09	22.04 ± 0.08	22.03 ± 0.08	16.80 ± 0.07	2.61 ± 0.02
P	0.09 ± 0.01	nd*	nd*	0.12 ± 0.01	0.25 ± 0.01	6.46 ± 0.03
S	0.39 ± 0.02	0.38 ± 0.03	1.10 ± 0.02	0.83 ± 0.01	1.49 ± 0.02	0.04 ± 0.01
Cl	3.05 ± 0.03	3.63 ± 0.04	0.23 ± 0.01	0.19 ± 0.02	2.42 ± 0.03	22.47 ± 0.08
K	1.23 ± 0.03	2.00 ± 0.05	2.34 ± 0.04	2.10 ± 0.03	1.53 ± 0.03	0.58 ± 0.02
Ca	5.88 ± 0.05	1.08 ± 0.05	3.97 ± 0.05	3.33 ± 0.04	1.97 ± 0.03	2.31 ± 0.03
Ti	nd*	0.43 ± 0.03	0.66 ± 0.02	0.26 ± 0.04	0.39 ± 0.02	0.17 ± 0.03
Mn	nd*	0.52 ± 0.06	0.32 ± 0.04	0.19 ± 0.04	nd*	nd*
Fe	1.50 ± 0.08	5.02 ± 0.15	6.42 ± 0.12	4.61 ± 0.11	7.70 ± 0.11	1.15 ± 0.07

nd = undetermined / under the detection limit*

In order to establish the quality of the investigated mud samples, was calculated the geoaccumulation index according with the scientific literature [24-26]:

$$I_{geo} = \frac{\log_2 C_n}{1.5 \cdot B_n} \quad (1)$$

where C_n is the measured concentration of the metals (n) in sediment; B_n is the concentration in average shale [27] of element n. The factor 1.5 was introduced to include possible variations of the background values due to lithogenic effects [27]. The obtained values for geoaccumulation index and the quality class of mud samples are presented in Table 2.

Table 2. Geoaccumulation index (I_{geo}) and muds quality class (QC).

Element	Samples					
	Persani	Grid	Homorod 1	Homorod 2	Rodbav	Rupea
Na	0.4181	0.3622	0.1115	0.1007	0.2957	-0.2144
Mg	-0.5997	-0.1441	0.0873	0.0046	0.1826	1.3543
Al	0.1914	0.2134	0.2197	0.2180	0.1948	-0.1021
Si	0.1017	0.1181	0.1190	0.1190	0.1085	0.0369
P	-15.4397	-	-	-13.5951	-8.8889	0.9624
S	-6.9664	-7.1586	0.7051	-1.3785	2.9503	-23.8146
Cl	0.5107	0.5905	-0.6731	-0.7606	0.4048	1.4254
K	0.0796	0.2667	0.3271	0.2854	0.1636	-0.2096
Ca	0.5875	0.0255	0.4573	0.3990	0.2249	0.2777
Ti	-	-1.7646	-0.8688	-2.8165	-1.9688	-3.7049
Mn	-	-0.9387	-1.6357	-2.3840	-	-
Fe	0.0600	0.2387	0.2751	0.2261	0.3020	0.0207
QC	Uncontaminated to moderately contaminated (I_{geo} = 0 – 1)					

Carbon and oxygen are missing from the Table 2 due to the fact that these elements are basic constituents of the biosphere, hydrosphere, and atmosphere, and according with reference table [24] B_n has no value assigned. As can be seen from Table 2, all analyzed samples correspond to the quality class of uncontaminated to moderately contaminated muds.

The presence of organic and inorganic compounds in mud samples were qualitatively identified from the FTIR spectra, the results being centralized for each sample in Table 3.

Table 3. Infrared absorption wavenumbers [cm^{-1}] and relative intensity of mud samples with vibrational assignments.

Wave number [cm^{-1}] & Relative intensity*												Vibrational assignments [28-33]
Persani		Grid		Homorod 1		Homorod 2		Rodbav		Rupea		
wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	
3325s	-	3367s	-	3351s	-	3339s	-	3337s	-	3327s	-	stretching OH (water)
2517w	-	-	-	-	-	-	-	-	-	-	-	C-O (carbonate in calcite minerals)
2097w	-	-	-	-	-	-	-	-	-	-	-	CH vibrations in humic acids
1795w	1795w	-	-	-	-	-	-	-	-	-	-	C-O (carbonate in calcite minerals)
1636s	-	1634m	1635w	1637m	-	1637m	-	1635s	1629w	1635m	1639w	H-O-H bending
1416s	1408s	1423w	1412w	1416w	1418w	-	1407w	-	1411w	1406m	1414m	C-O (carbonate in calcite minerals)
1221w	-	-	-	-	-	-	-	-	-	-	-	Si-O bond (in silicate mineral)
1161w	1161w	-	-	1162w	1163w	1161w	-	-	-	1162w	-	S-O (sulphate); Si-O (in biogenic silica)
1007s	1028m	998s	1002s	988s	989s	991m	986s	1000w	1001s	1005s	1001s	S-O stretching (gypsum)
912w	-	912w	914w	912w	-	911w	-	913w	-	913w	-	Al-OH deformation (kaolin/montmor)
871s	872s	872w	873w	872w	874w	871w	874w	873w	875w	870m	872w	C-O (carbonate in calcite minerals)
-	-	829w	-	832w	-	826w	-	-	-	-	-	Al-O-H bend (montmor)
-	797w	-	795w	-	793w	-	-	-	795w	-	797m	Si-O (quartz, feldspars or clay minerals)
-	779w	-	777w	771w	776m	-	775m	-	778w	-	778w	Si-O (quartz)
		743w	-	744w	-	-	-	-	-	-	-	Si-O (quartz)
709w	712s	-	-	-	-	-	-	-	-	-	712w	Ca-O bond (carbonate)
-	696w	-	693w	690w	693m	-	692w	-	693w	-	694w	Si-O (quartz)
-	-	682w	-	680w	-	678w	-	-	-	-	-	S-O bend (gypsum)
-	-	639w	649w	-	647w	-	646w	625w	630w	-	635w	Si-O-Si bending (feldspar)
515w	515w	514w	518m	517w	521w	515w	519w	512w	518w	512w	518w	Al-O-Si bend (feldspar)
-	461m	-	463w	-	-	-	-	-	462m	-	462m	Si-O-Si bending (quartz / illite)
455w	-	-	-	-	456w	-	-	-	-	-	-	α-FeO(OH) (goethite)
-	-	-	-	444w	444w	431w	-	448w	449w	448w	-	SiO4 symmetric stretch (kaolin)
423w	426w	-	424w	420w	-	-	421w	-	424w	-	-	Ti-O bend (rutile)

** s-strong; m-medium; w-weak.*

Table 3. (*continued*)

Wave number [cm^{-1}] & Relative intensity*												Vibrational assignments [28-33]
Persani		Grid		Homorod 1		Homorod 2		Rodbav		Rupea		
wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	
-	-	418 w	-	413 m	415w	410 w	-	416 w	-	415 w	419 m	Si-O (in biogenic silica)
397 w	-	-	-	-	-	-	392w	-	396 w	-	392 w	α-FeO(OH) (goethite)
383 w	-	-	386 w	385 w	388w	387 w	-	385 w	-	388 w	-	α-FeO(OH) (goethite)
375 w	-	375 w	375 w	371 w	364w	367 w	-	371 w	370 w	369 w	367 w	Si-O bend (quartz)
-	355 w	359 w	355 w	359 w	-	355 w	358w	356 w	-	-	357 w	O-H-O bend (kaolin)

** s-strong; m-medium; w-weak.*

The band between 3367 and 3327 cm^{-1} is due to CH-vibrations from $-CH_3$, $-CH_2$ and -CH groups present in organic compounds (humic substances, mainly humic, fulvic and humic acids, present as a sharp peak in wet samples). Bands centered at 1630 cm^{-1} in wet samples are attributed to the vibration group C = O stretch of said organic compounds. These values are also found in dry samples, proof that the double bond in the aldehyde or ketone groups (-C=O) is not destroyed by drying the samples. Calcium carbonate has molecular vibrations around 710, 870, and 1400 cm^{-1}, and silicon dioxide in biogenic silica has a significant maximum absorbance of 1000-1007 cm^{-1}, combined with values around 500 cm^{-1}.

These values are found in both wet and dry samples, demonstrating that they are not destroyed by drying. Values around 1162-1160 cm^{-1} of wet samples are attributed to the -OH groups in the glucose structure or benzene cyclic, which are mostly destroyed at temperature. The FTIR can thus provide information on organic and inorganic compounds (e.g. carbohydrates, humic substances, silicates, and carbonates).

The fact that the mineral water springs and the therapeutic mud areas are located, most of them in the outskirts of their localities (e.g. Grid, Homorod, Rodbav etc.), in these areas can be arranged spas or recreational complexes that address primarily villagers and potential tourists from other parts of the country. Last but not least, it is necessary to mention the type of bioclimate, which for most of the localities with mineral springs in the county is the sparing.

4. CONCLUSIONS

For Brasov County, the balneary potential, spa treatment (therapeutic mineral waters and therapeutic sludge) can be classified as inexhaustible natural resources and, as a result, spa tourism can be practiced permanently. The spa tourism development projects, especially in the former spa centers of local importance (e.g. Persani, Homorod and Rodbav - where there is also therapeutic mud), should also take into account the therapeutic potential of the localities nearby, such as Grid (where there is an important source of therapeutic mud).

In this study were analyzed six mud samples in order to identify if the sites can be re-entered in the balneary circuit. By SEM-EDS was proved that the mud samples are clean and just few algae were identified. Also, the EDS data show the presence of some elements (e.g. C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, and Fe), but the geoaccumulation index has values in the range of 0-1, which includes the analyzed samples in the category of uncontaminated to moderately contaminated muds.

FTIR technique was widley used on this study in order to investigate the molecular-level processes at mineral, organic, and bacterial surfaces of mud, a point of start for further research concerning determination of their influence on biogeochemical cycles of elements. Furthermore, by this study, it was demonstrated that FTIR spectra contain significant information on mineralogical as well as organic constituents in mud samples.

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