INVESTIGATION OF SOME THERAPEUTIC MUDS COLLECTED AT DIFFERENT SITES IN ROMANIA: PRELIMINARY RESULTS

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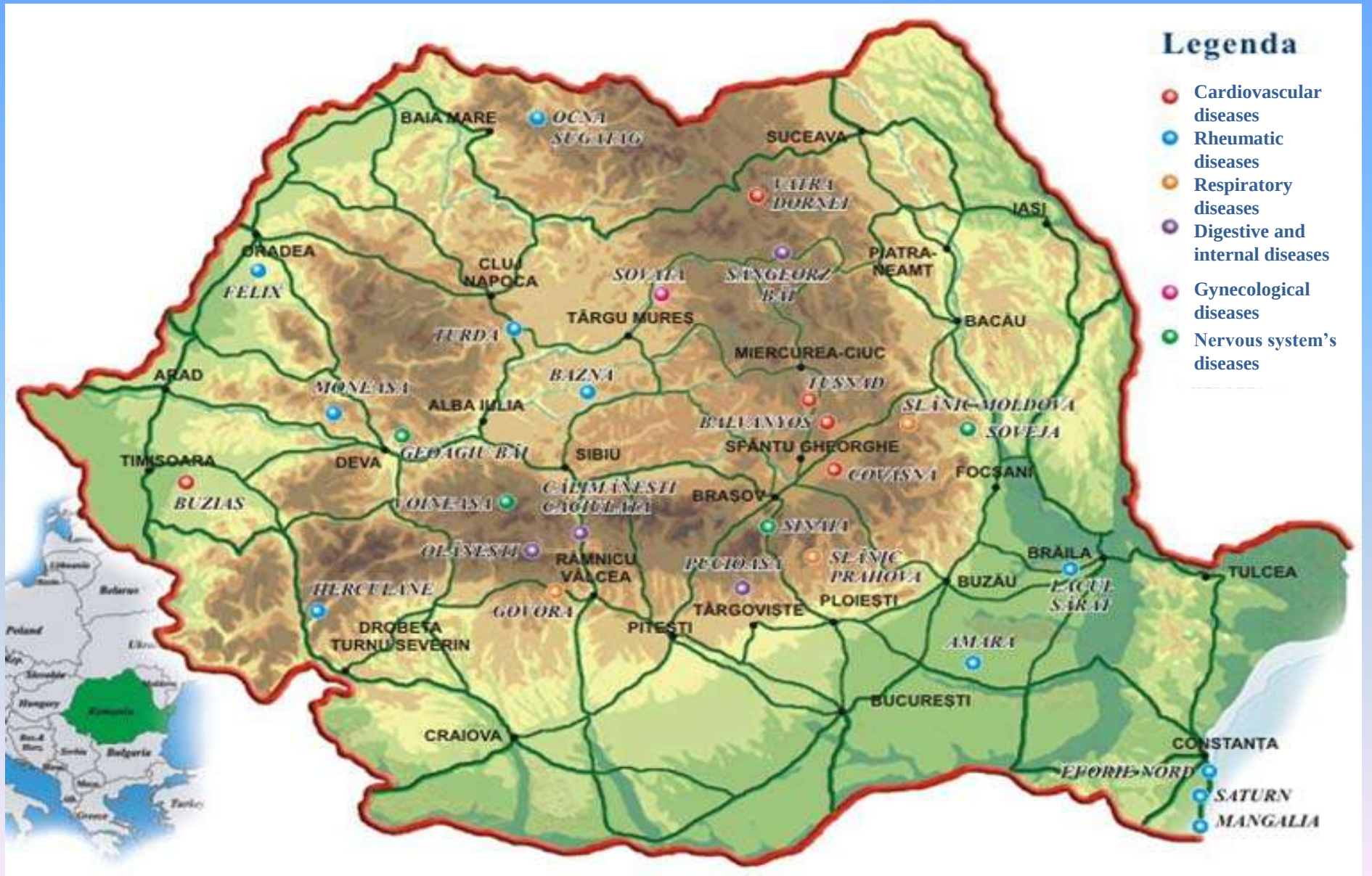
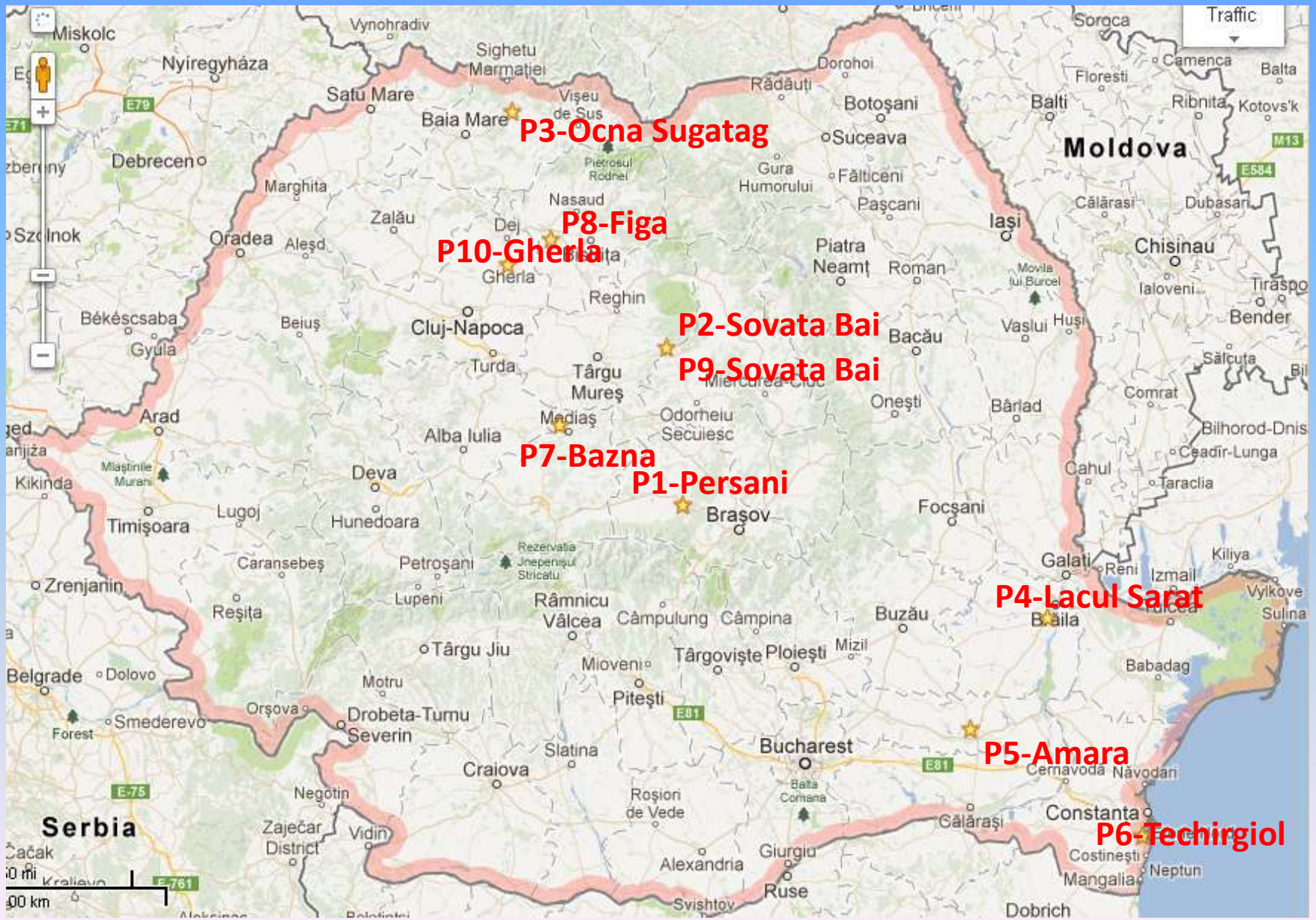
A long history of balneology at the Romanian territory

Roman thermae in Herculane (South-West of Romania)

Romania owns 30% of the European balneary resources



The sampling sites of the therapeutic muds



Preliminary sample preparation

Sapropelic muds - unconsolidated oozes consisting mainly of putrefied plant remains and found in anaerobic areas at the bottom of swamps, lakes, and shallow seas

- dried at 120 ^{o}C in oven in presence of air for 5 hours
- grinded
- sieved through a plastic device in order to separate both the particles and the vegetal remains
- separated by fractions : coarse and vegetal remains

The analysis has been performed only on the fine fraction that represented at least 95 % of the dried sample weight.

coarse particle fraction

vegetal remains

Instruments and methods

Differential scanning calorimetry

Setaram 131 evo

The non-isothermal (ramp) measuring mode has been applied in this study, using either inert (nitrogen) or oxidative (air) atmosphere.

- gas flow - 50 mL/ min.
- heating rate -10 K/min.

The **oxidation onset temperature** OOT values as well as the other parameters characterizing the different processes (such as the oxidation or the decomposition), namely Tmax (**the temperature in the maximum**, of the peak) and ΔH (**the thermal effect of the process**) were obtained from non-isothermal differential scanning calorimetric **(DSC)** measurements in air, using the procedures described in international standards for organic compounds.

The organic content

$$C = \frac{m_o - m_f}{m_o} \cdot 100$$

Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR spectroscopy)

ATR Jasco Pro 470-H

FTIR-Jasco 4200 spectrometer

- resolution 2 cm^{-1}
- 48 scans/each spectrum

Energy Dispersive X-Ray Fluorescence (EDXRF)

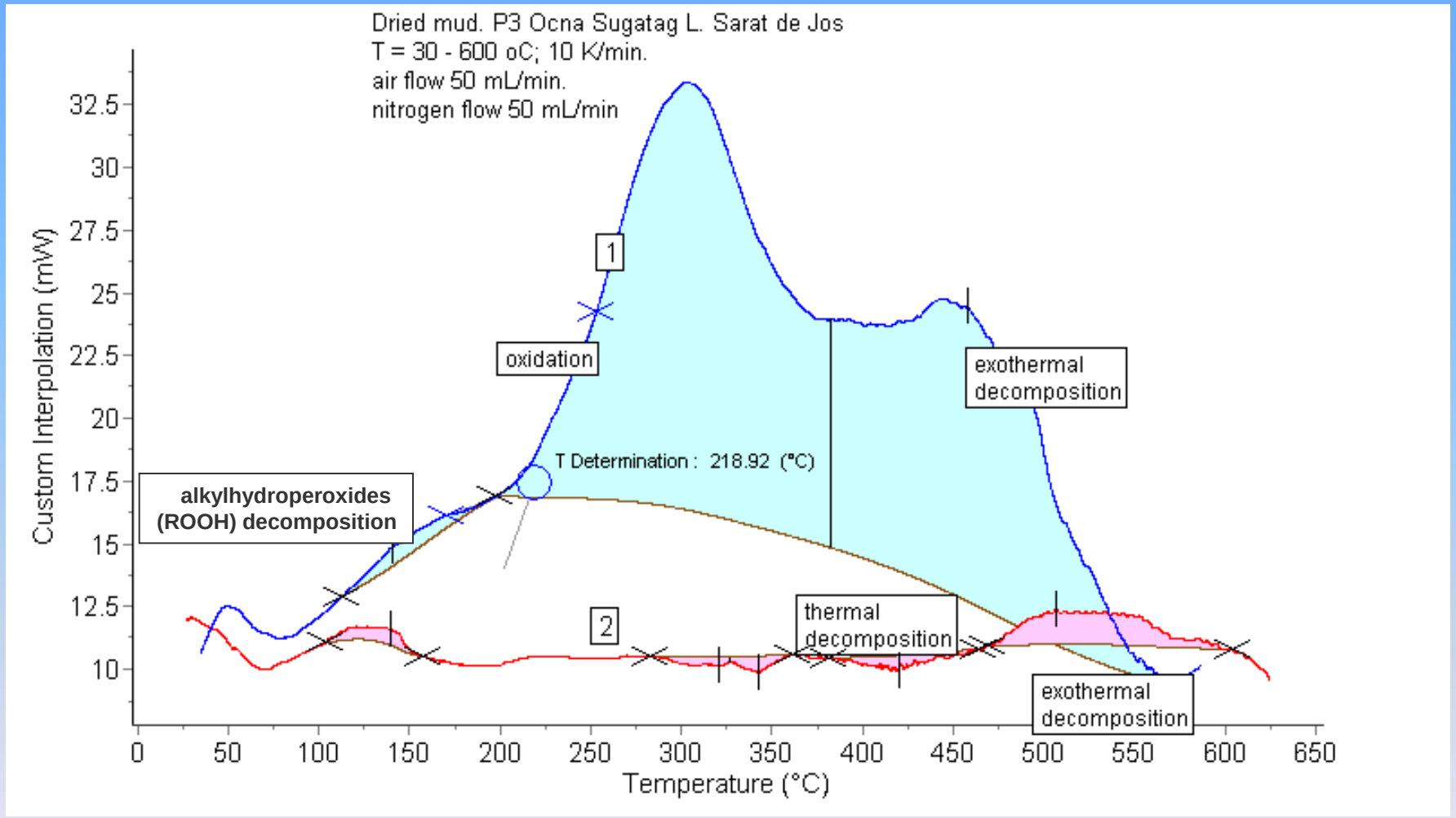
ElvaX Ligt XRF analyzer (Elvatech, Kiev, Ukraine)

- EDXRF analysis directly on dried mud samples
- mass of sample ~ 3.4 g
- the irradiation time: 30 minutes
- calibration:
  - Yb standard solution added directly to mud matrix
  - different simpler compounds and their mixtures with known concentrations.
- comparative XRF measurements on selected samples at the Laboratory of Mechel s.a. Targoviste.

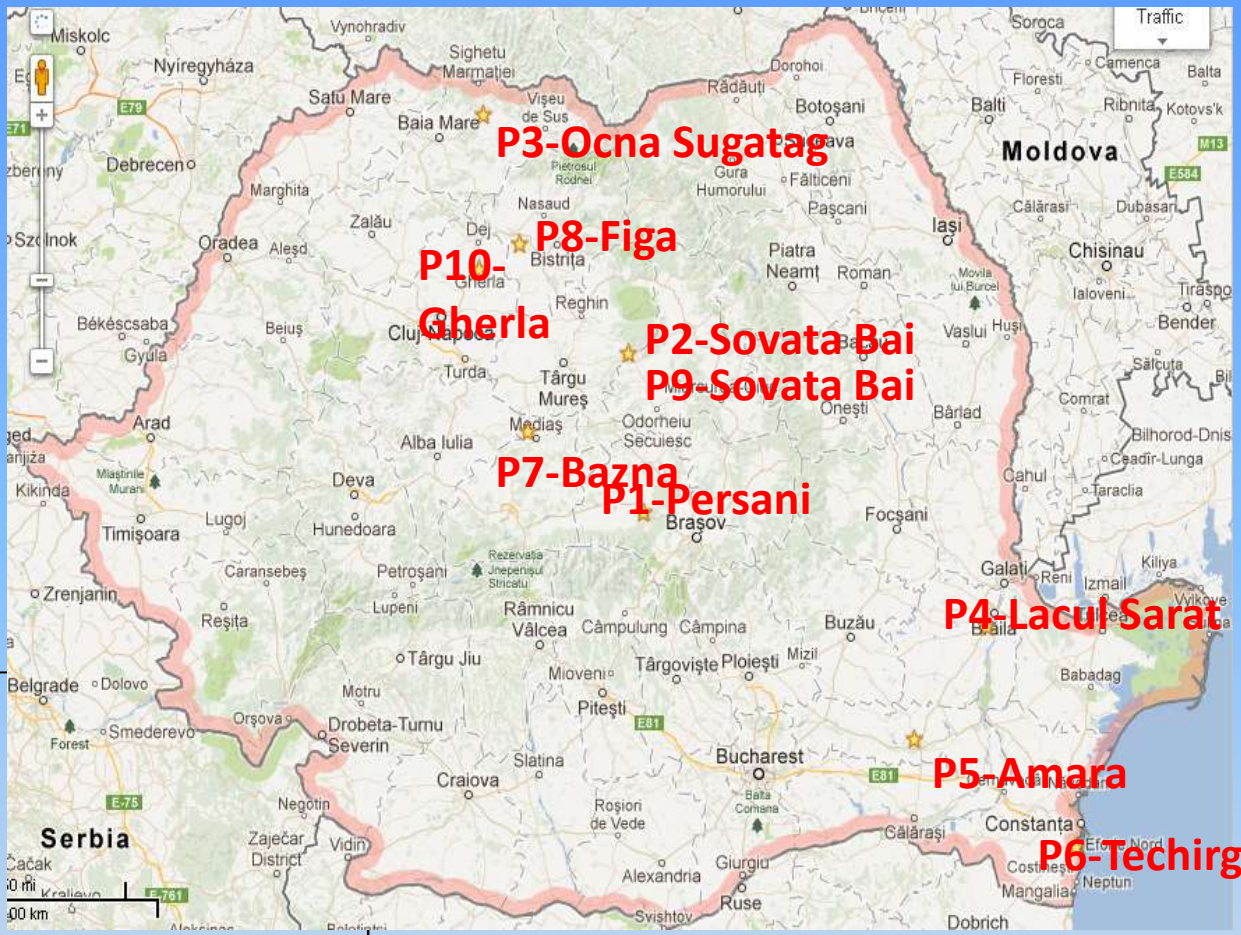
Instrumental Neutron Activation Analysis

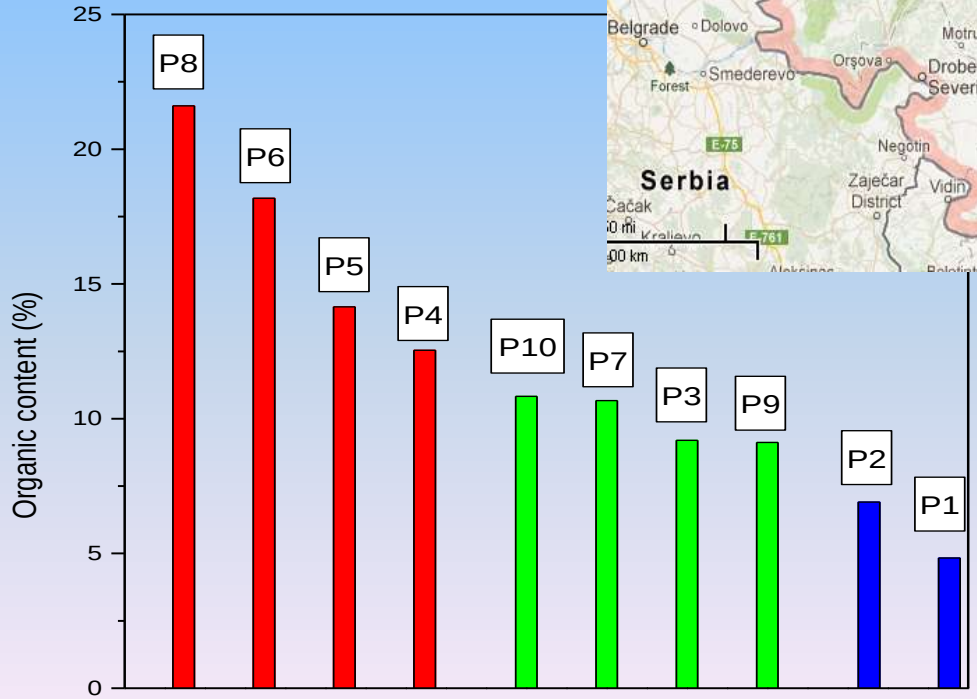
- short term irradiations: 60 s
- long term irradiations: 63 h
- comparator method was used employing standard reference materials 1633b, 2709, 2710, 2711 and 433
- final uncertainties between 3 % for Na, Al, Zn and As and 41 % for I
- a total of 37 elements were determined

Thermal analysis

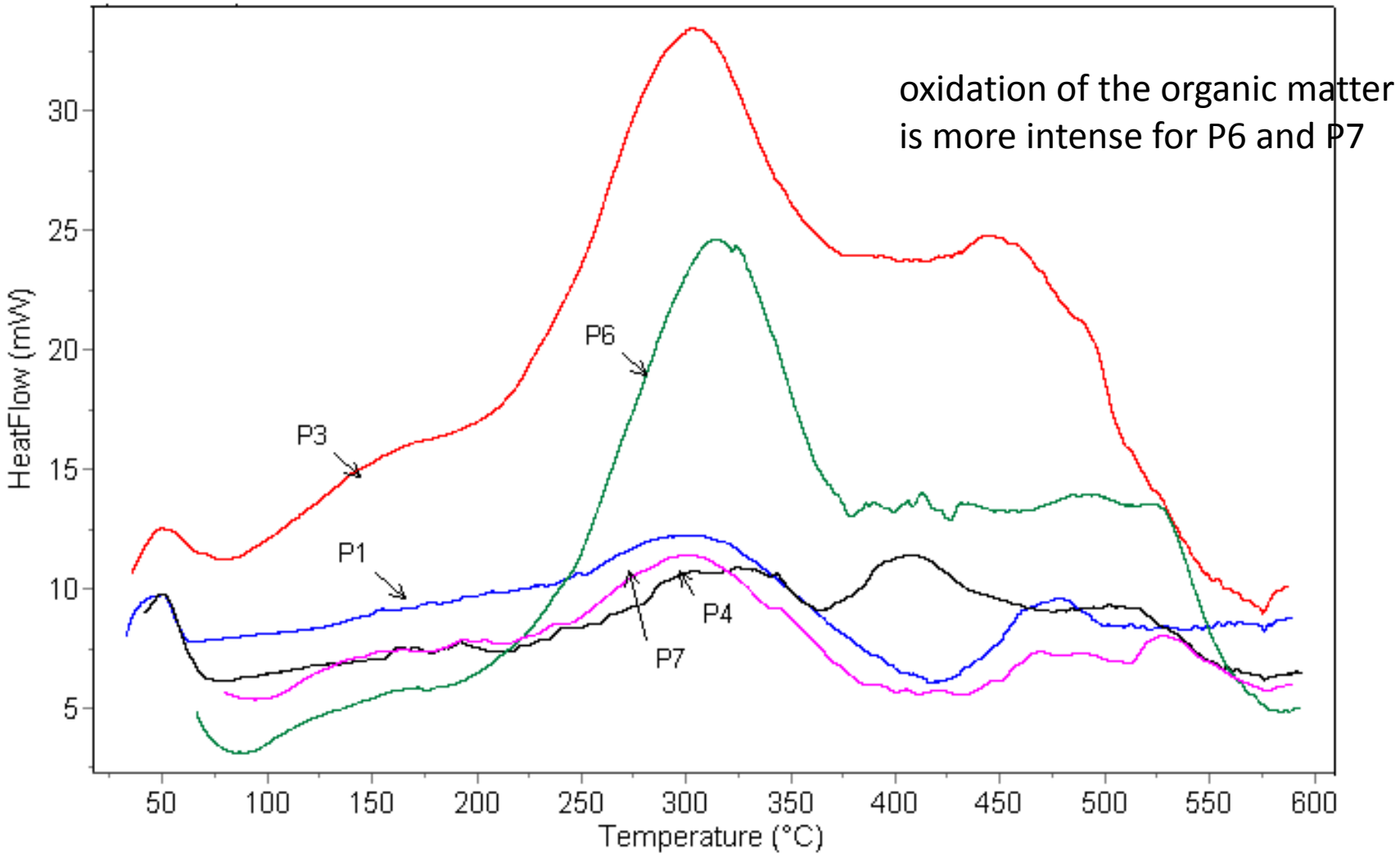


DSC curves of dried muds from Ocna Sugatag (L. Sarat de jos, sample P3) in air (1) or in nitrogen atmosphere (2). Heating rate: 10 K/min.





Ranking of the mud samples as a function of their organic content

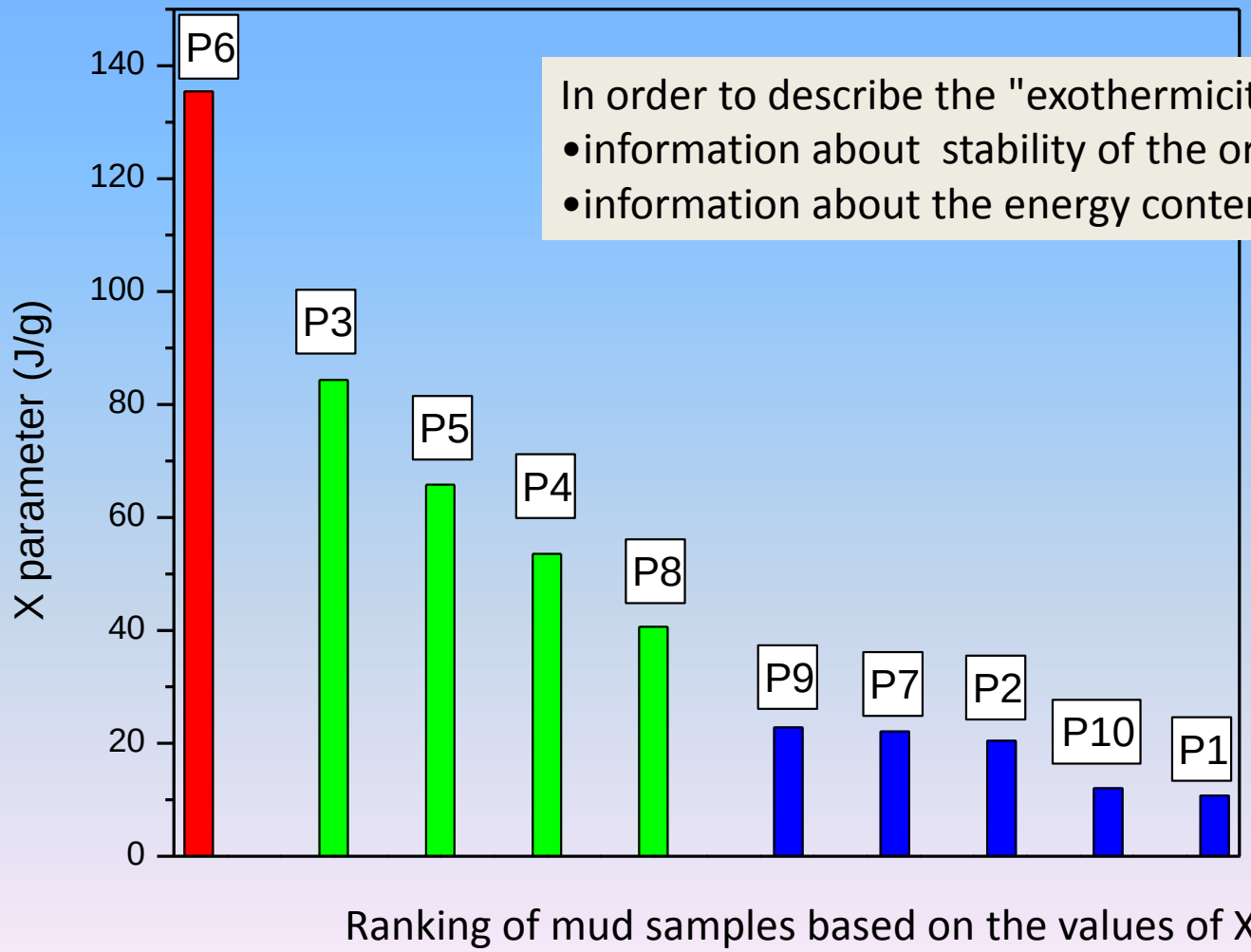


Comparative differential scanning calorimetric curves of different muds

$$X = - C \cdot \Delta H_{exo}$$

C - the organic content

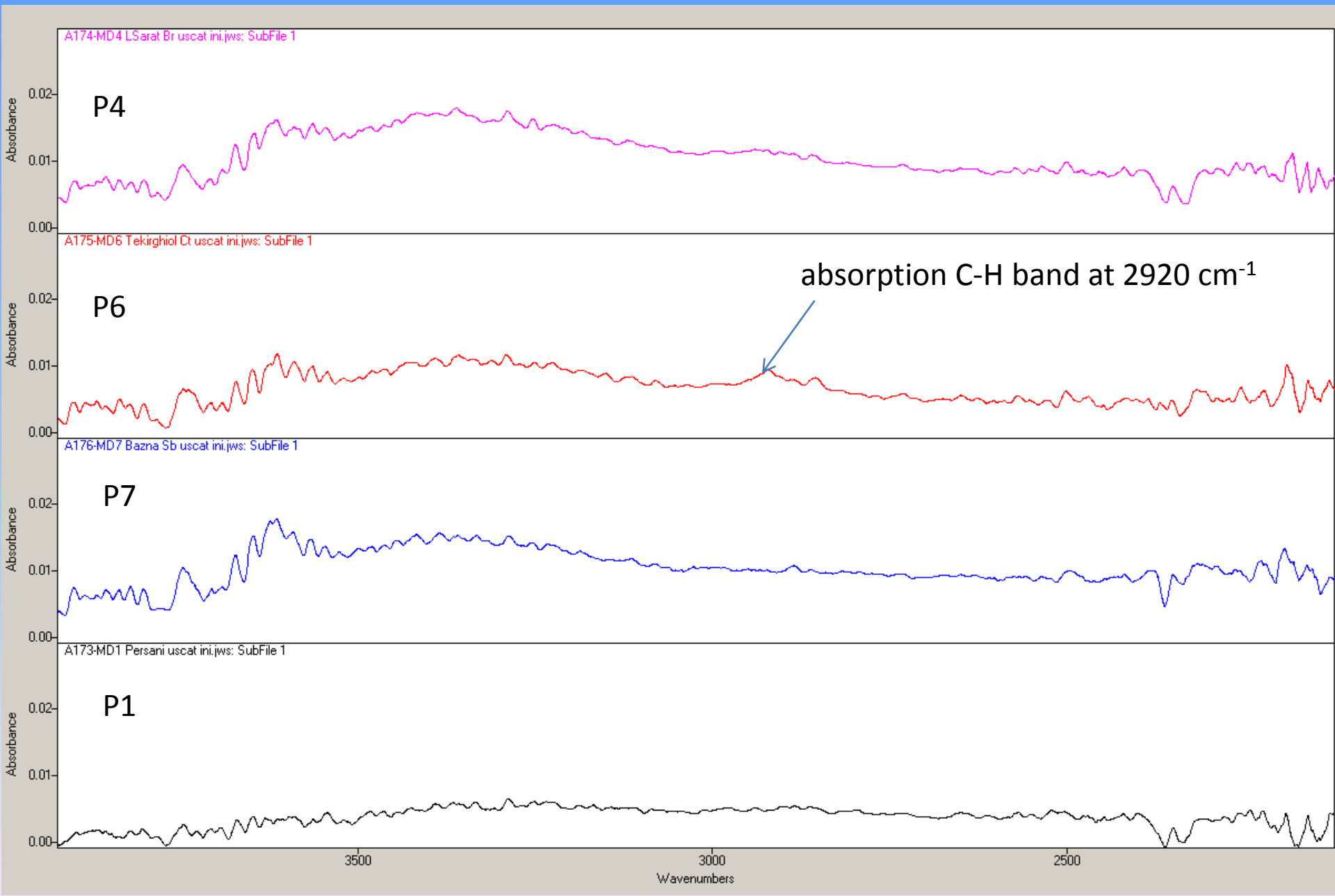
ΔH_{exo} - the sum of the thermal effects of oxidation and decomposition (the exotherm processes)



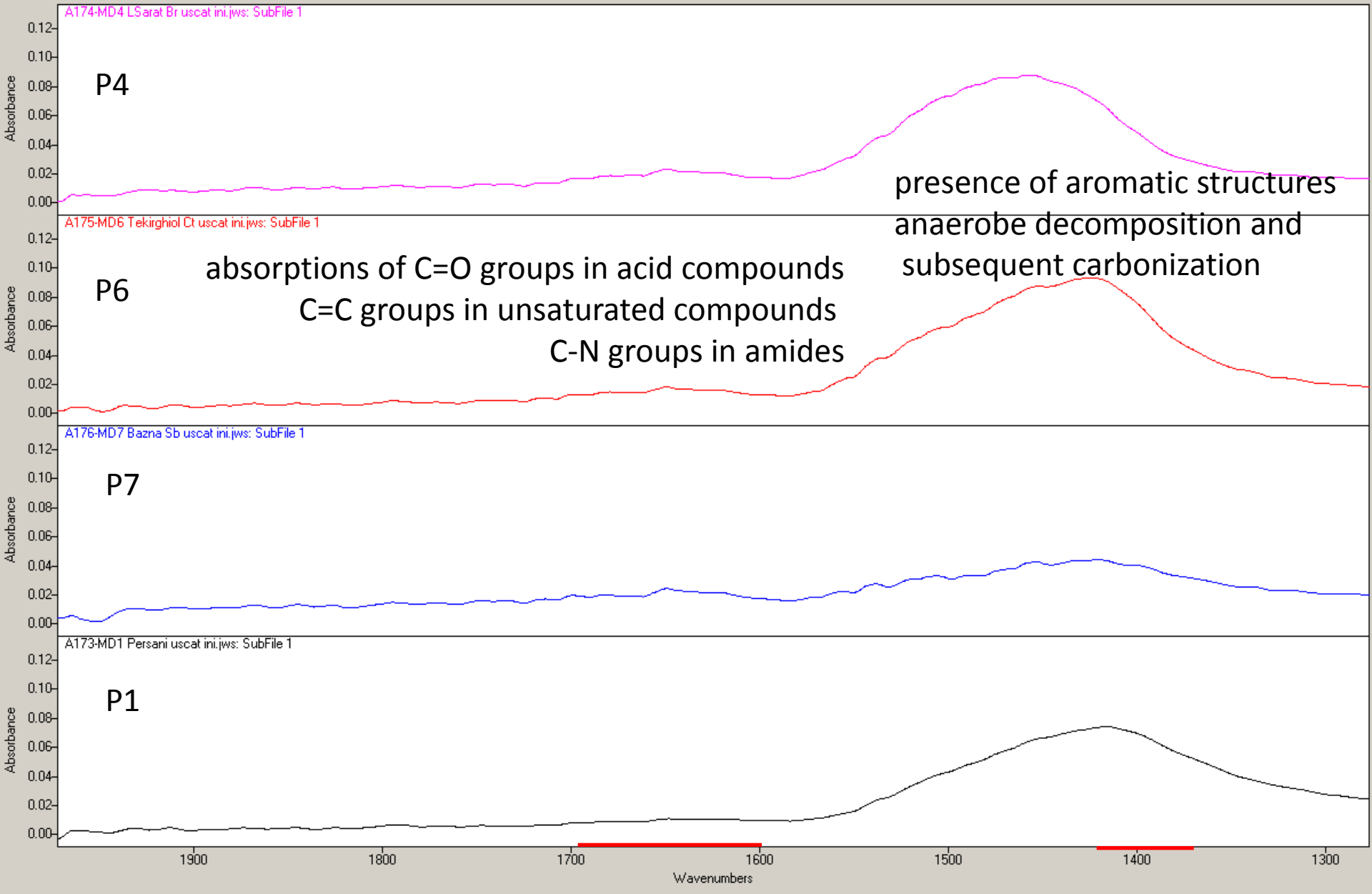
In order to describe the "exothermicity" of a material:

- information about stability of the organic-inorganic composite,
- information about the energy content of such a composite.

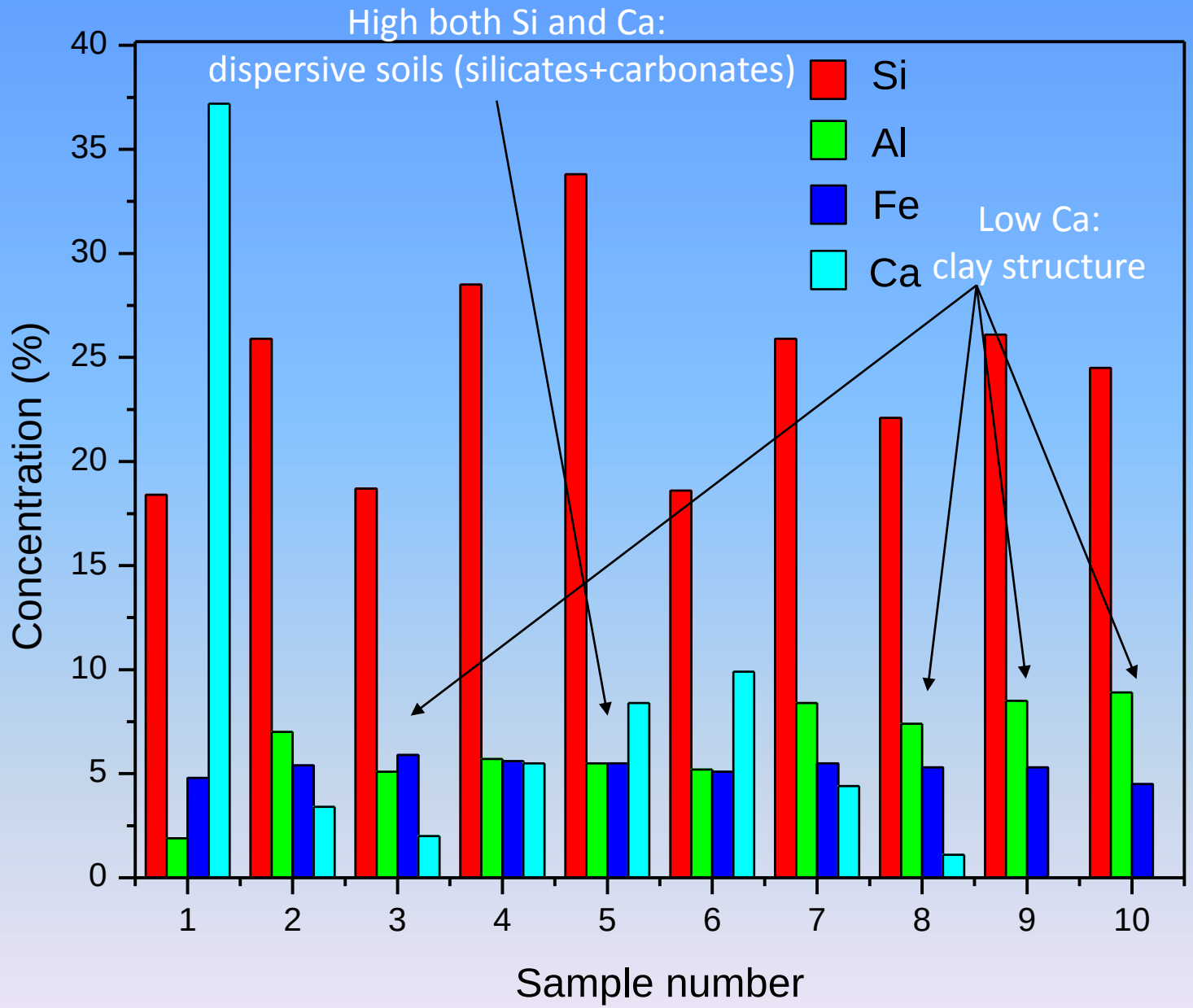
Ranking of mud samples based on the values of X parameter



ATR-FTIR spectra in the region 4000 - 2000 cm^{-1} of some mud samples (in dried state)



ATR-FTIR spectra in the region 2000 - 1200 cm^{-1} of some mud samples (in dried state)



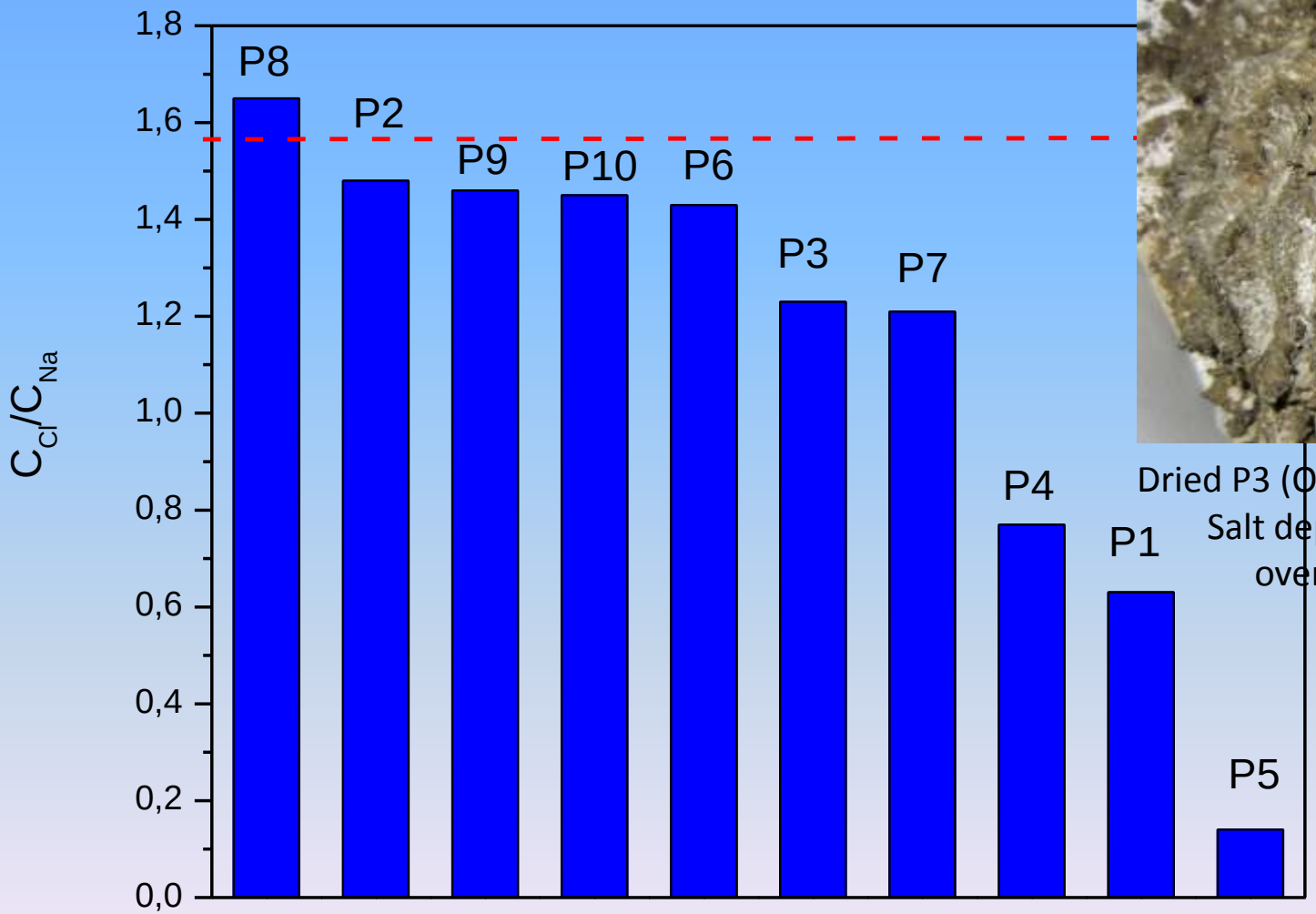
Comparison of the Si, Al, Ca and Fe content of the studied mud samples obtained by EDXRF

Results of INAA elemental analysis of the studied mud samples

The highest concentration of Ca

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

Ratio < 1.54: a) other anions (e.g. sulfate, carbonate) in important amounts
b) inclusion of sodium ions in the mineral matrix
Ratio > 1.54: occurrence of different chloride salts (with Mg or Ca)



Ratio m_{Cl}/ m_{Na} for the studied mud samples.
The red line corresponds to the value for sodium chloride (1.54)

Dried P3 (Ocna Sugatag) mud sample. Salt deposits are visible after oven-drying treatment

Results of INAA elemental analysis of the studied mud samples

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

> WL

C≈2NL< WL

NL<C<WL

C>WL for sensitive soil applications

Results of INAA elemental analysis of the studied mud samples

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

NL<C<WL

C< NL

Conclusions

1. 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.
2. 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, hydrophylity, antioxidant activity a.s.o.
3. The studied muds are generally rich in sodium being formed in the presence of salted water.
4. Other elements are also present, but their concentrations are generally inside of the normal limits for the soils

Conclusions

5. 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.
6. Increased concentrations of As found for some samples can be related to the specific natural conditions of geothermal areas.
7. Further work will be devoted to 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 and their correlation with curative proprieties of the muds.
8. A comparison of data obtained with those from literature should be done, too.

Acknowledgements

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Thank you!