

## CHARACTERIZATION AND ORGANIC COMPOUNDS IN PELOIDS FROM MONGOLIA

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### Abstract

The peloids are the important natural remedy all over the world. The physicochemical properties and some organic matters of peloids from 12 lakes in Mongolia were examined. These peloids belong to the continental hydrosulfide sticky peloid except Gurvan nuur peloid. Peloid from Lake Gurvan nuur was classified as a sapropel with high ash content.

The peloid organic matters were investigated using chemical analysis and several analytical techniques, such as IR, and <sup>13</sup>C NMR spectroscopy, GC/MS, gas chromatography. The concentration of total organic carbon in all continental hydrosulfide sticky peloids is ranged from 0.4% to 3.1%, but 15.3% in the sapropel. It shows that the majority of the peloids in Mongolia are hydrosulfide sticky peloid with lower organic matters than the sapropel and peat. In this study, no significant difference of chemical composition was observed between dissoluble and insoluble organic matters from peloids. Some classes of biomolecules, including lipid and carbohydrate, were identified. Biogenic stimulator humic acid (HA) is the major part of the peloid organic matter. HA concentration varied between 11.2% and 55.9% of total organic matter of peloids. The macromolecule of the sapropel HA exhibited a lower aromatization degree and more functional groups than other HAs, as revealed by the <sup>13</sup>C NMR data and C/H ratio. The genesis of peloid organic matter is discussed in this paper.

Our results suggest that the presence of known bioactive organic compounds, such as humic acid, lipid, and carbohydrate, as well as hydrogen sulfide causes the balneological value of peloids in Mongolia.

**Keywords:** lake; organic matter; peloid

## 1. Introduction

Peloids are a multi-component system, which consists of mineral water, clay minerals, organic matter and organo-mineral complex, and applied for healing procedure. In 1807, the first chemical analysis of peloids was performed by French chemist Dessier (Ivanov and Malakhov, 1963). Various types of peloids differ in concentration of organic matter and its composition. Recently, the use of healing mud in pharmaceutical formulations, spas and aesthetic medicine increased due to increasing interest and success of natural remedies (Veniale et al., 2007). Nowadays, manmade peloids that obtained by mixing mineral water and clay (Veniale et al., 2004), as well as matured peloids after its application for therapy are widely used in many sanatoriums (Veniale et al., 2007). In this text, the term *peloid* refers to the natural healing mud, which is collected from the lake-bottom.

According to the conventional point of view, the therapeutic action of peloids is due to their thermal-, chemical- and mechanical properties, and hence, the thermal behavior of clay materials has been intensively studied (Cara et al., 2000; Legido et al., 2007; Ferrand and Yvon, 1991). During pelotherapy, a certain part of chemical components penetrate the skin by diffusion and electrophoresis. This concept had been demonstrated by using the Franz-type diffusion cells (Tateo et al., 2009). The mechanical particles in peloid induce mechano receptors in derma, which cause the recipient to experience the thermal and chemical effects (Vaisfeld and Galina., 1996). However, this is a limited approach to understanding the healing effects of peloid and usually emphasizes it due to heat. A lack of the fundamental research material of peloids in Mongolia results in scarce scientific background in the peloid application.

Russian scientists carried out extensive research on the chemical nature and therapeutic properties of the sapropel and peat (Bakhman and Ovryanikova, 1965; Puntus, 1998, 2008; Shinkarenko and Milenina, 1981; Shustov, 1996). There are many biogenic stimulators produced from peloids, including *Peloidsilt*, *Peloidodistillate*, *Torfortum*, *Humisol*, as well as other medical preparations based on peloid organic and inorganic fractions (Mashkovsky, 1993).

Organic matter represents 82-94% of peat, 15-80% of sapropel, 1-5% of hydrosulfide sticky mud and less than 0.5% of pseudo-volcanic mud (Ivanov and Malakhov, 1963; Tsarfis and Kiselev, 1990). Humic acid (HA) is a major part of peloid organic matter. In sapropel, HA stimulate the macrophage defense reaction, promote nervous tissue regeneration, stimulate tissue reparation, and produce anti-inflammatory effect in case of tissue burns and cornea diseases (Degtyarenko and Mokulkin, 1997). In addition, HA is the known complexing ligand of trace elements, this is also possible to form complexes with amino acids, peptides, carbohydrates and steroids, which may be responsible for some of the effects occurring in tissues, including the elimination of heavy metals, desmutagenic effects, antioxidant and anticoagulant activity.

There are more than 40 lakes with healing mud in Mongolia. The physiochemical characteristics and chemical nature of peloid may be differ due to their various origins and

healing effects. The study of the organic matters from hydrosulfide sticky peloid is poorly addressed. The geochemical and mineralogical composition, the radioactivity of several natural nuclides of the analyzed peloids, and trace element concentration in the organic extracts were investigated earlier (Tserenpil, 2005).

The main objective of this paper is to determine the chemical composition of organic matters from natural healing mud in Mongolia, and to provide some fundamental data which are useful to explain the therapeutic effects of peloid. On the other hand, it is necessary to define their chemical composition, particularly, organic matters for peloid maturation process. This process is strongly influenced by microbial activities and the availability of organic components (Carretero et al., 2006; Tateo et al., 2009).

## 2. Materials and methods

### 2.1. Sampling area

Peloid samples were collected from 12 lakes located in Central, Eastern and Western provinces of Mongolia, including the following: Lake Avagra toson (geographic coordinates are 43°13' N; 109°31' E) and Lake Gurvan nuur (42°01' N; 111°40' E) (in Khentii province), Lake Ikh tsaidam (47°04' N; 107°41' E), Lake Bus (47°45' N; 106°50' E) and Lake Olziit (46°58' N; 106°50' E) (in Central province), Lake Zegstei (in Sukhbaatar province), Lake Utaat mijuur (48°43' N; 115°05' E) and Lake Hotont (in Dornod), Lake Uud (46°20' N; 101°14' E) (in Bayankhongor), Khujirt (in Uvurkhangai), Lake Darday (49°39' N; 106°02' E) and Lake Shargiin tsagaan (in Selenge province).

Peloids from Lake Avarga toson, Uud and Khujirt are used in the sanatoriums by preparing a mixture of mud and natural mineral water called-Rashaan.

### 2.2. Methods

Sediments were collected separately into pre-cleaned wide-mouth glass bottles of 500-1000 ml volume and lake surface water was retained at the top to prevent an oxidation of sediments. The sediments were refrigerated (4°C) at laboratory until analysis.

The characteristics of peloids were determined according to Shukarev method (Bakhman and Ovsyanikova, 1965). Data were normalized to dry weight after desiccation at 105°C, until weight stabilization. Biogenic silica was measured by spectrophotometer after samples were digested in a 2 M Na<sub>2</sub>CO<sub>3</sub> solution at 85°C for 5 hours in plastic vessels. For the determination of dissolved sulfide, sulfide was first volatilized adding acid by converting it to gaseous hydrogen sulfide (H<sub>2</sub>S). H<sub>2</sub>S was purged from samples by carbon dioxide and trapped in an iodine solution, which was reduced by hydrogen sulfide. Sodium thiosulfate was used as a titrant to verify the sulfide concentration iodometrically. The concentration of total organic carbon (TOC) was determined using rapid dichromate oxidation of organic matter (Nelson and Sommers, 1996). The concentration of total organic matter (TOM) was evaluated by TOM=TOC·1.72 equation. The pore water was

separated from peloids by a simple pressing device.

Distilled water and organic solvents were used for extraction of organic matter. The solvents were evaporated by a rotary vacuum evaporator. HCl was used to release the organic matters associated with carbonate minerals. The lipid fraction was extracted with a mixture of chloroform/ethanol (1:1) (Dolmaa et al., 2004). Humic acid (HA) was extracted with 0.2 N NaOH aqueous solution after demineralization of peloid. The carbohydrate extract was obtained by water extraction at 40-50°C and purified using a dialysis bag. The extract was freeze-dried for future analyses. This study involved identification of the different fractions of organic matter from peloids by IR and <sup>13</sup>C NMR spectroscopy, GC/MS, gas and gel chromatography. IR spectra were recorded on spectrometer IR-20 using a KBr pellet. GC/MS, of the organic extracts of peloid, are taken on HP 5971A mass spectrometry using capillary columns packed with BD5, OV70-280, SE-54, and SE-30 25 or 60 m long in a automatically programmed temperature schedule at 4 K/min. Individual organic compounds were identified with reference to standard electronic libraries of mass spectra (chromatographic retention indices): NIST 21, NIST 98, NIST 107, PMW tox 3, Wiley 229, Wiley 138, and NBS 75K. Spectra with at least 85% similarity were chosen. For dialkyl phthalates identification we selected spectra with a resemblance coefficient no lower than 95%. <sup>13</sup>C NMR spectra were acquired on spectrometer Varian VXR 500S with working frequency of 125.1 MHz for nuclei <sup>13</sup>C in solution dimethyl sulfoxide, mode INVGAT and time of scanning 24 hours. For the identification of monosaccharide composition, we used gas-liquid chromatography. Trichloroacetic acid was used for protein analysis as a precipitating agent.

### 3. Results

#### 3.1. The general characteristics of peloids

The physicochemical characteristics of sampled peloids are reported in Table 1. Based on their properties, peloids were classified by the national standard (Dolmaa et al., 2008) due to the lack of normative regulations about quality standards and non-existing international classification for peloids (Veniale et al., 2004). The moisture content varied from 10.48 to 55.95%, which was lower compared to organic rich peloids (60-80%). Most peloids are dense 1.43-1.9 g/cm<sup>3</sup> (excluding those from Gurvan nuur), and healing materials for pelotherapy may be prepared by mixing with mineral water. The concentrations of TOM were usually lower than the peat and sapropel, but higher than pseudo-volcanic peloid. For instance, TOM concentration varied between 0.74-5.4% in peloid samples, while the concentration was 26.32% in peloid from Gurvan nuur. Peloid H<sub>2</sub>S level was high (up to 0.89%) and resembles to the concentration for continental hydrosulfide sticky peloids.

From Table 1, the studied healing muds are typical of the continental hydrosulfide sticky peloids (except peloid from Lake Gurvan nuur) and were classified into the following subgroups based on by mineralization and sulfidation. Peloids from Lake Olziit,

Khotont and Lake Ikh tsaidam were highly mineralized (pore water mineralization was 67.8-215.5 g/L) and medium sulfidation type, Lake Zegstei, Bus, Darday and Khujirt's peloids are low mineralized (15.8-19.7 g/L) and high sulfidation; peloids from Lake Avarga toson and Utaat minjuur are low mineralized (10.7-12.1 g/L) and low sulfidation. Peloid from Lake Gurvan nuur dramatically differed from other mud samples in moisture content (55.95%), high concentration of TOC (15.30%), lower content of particles with diameter more than 0.25 mm (0.46%), and pore water mineralization (3.8 g/L). The results indicate that Gurvan nuur peloid was formed in low-mineralized water and therefore was classified as sapropel peloid with high ash content (67.46%).

Table 1.

The general characteristics of peloids in Mongolia

Peloids from Lake	Moisture, %	Density, g/cm <sup>3</sup>	Mineralization pore water, g/L	Content, % (dry weight, dw)				
				TOC	TOM	Si <sub>bio</sub>	Particles > 0.25 mm diameter	H <sub>2</sub> S
Avarga toson	37.84	1.55	10.7	2.83	4.87	0.45	4.72	0.03
Bus	44.65	1.53	16.0	3.14	5.40	0.50	5.25	0.89
Darday	45.47	1.43	19.3	0.43	0.74	0.09	15.77	0.21
Ikh tsaidam	33.60	1.75	140.6	1.30	2.24	0.15	14.78	0.30
Gurvan nuur	55.95	1.13	3.8	15.30	26.32	0.87	0.46	0.05
Khotont	32.58	1.65	67.8	0.91	1.57	0.62	7.86	-
Khujirt	27.60	1.78	19.7	2.15	3.70	1.07	1.97	0.24
Olziit	29.06	1.90	215.5	1.06	1.82	0.26	3.28	0.25
Utaat minjuur	27.14	1.73	12.1	2.44	4.20	0.49	24.82	0.03
Uud	37.87	1.74	163.9	2.60	4.47	0.04	9.80	0.86
Shargiin tsagaan	10.48	1.64	58.7	1.27	2.18	0.13	2.50	0.03
Zegstei	26.99	1.73	15.8	0.62	1.07	0.08	5.66	0.21

H<sub>2</sub>S possesses important physiological and pharmacological functions in the regulation of blood pressure (Rui Wang., 2002), and its content varied between 0.03 and 0.89% in dry peloids. The increase in the availability of reactive organic matter promotes H<sub>2</sub>S formation through anoxic bacterial reduction of salt water sulfate (Allison et al., 1991). This positive correlation between organic matter and sulfide was also observed in these lakes, with higher organic content associated with higher sulfide (Table 1). The maximum concentrations of H<sub>2</sub>S were 860 mg and 890 mg/100 g peloid in Lake Uud and Bus, respectively. The TOM concentrations were 4.47% and 5.4% in above mentioned peloids.

### 3.2. Dissoluble and insoluble organic matters from peloid

Dissoluble organic matter (DOM) and insoluble organic matter (IOM) isolated from peloids ranged from 0.37-15.51 mg/g and 0.84-12.93 mg/g, respectively (Table 2). The distribution and bruto-formula of individual organic compounds in DOM and IOM are summarized in Table 3.

GC/MS chromatogram of dissoluble organic matter (DOM) from peloids in Lake Avarga toson is shown in Fig.1. DOM of peloids was comprised of 58.38-66.67% C, 6.55-9.89% H, 0-1.83% N, and 0-4.05% Cl (Table 2) which indicated the presence of heteroatom compounds in the organic extracts. The hydrocarbons were minor constituents (0.52-4.66%) in DOM from lakes Avarga toson, Ikh tsaidam, Utaat minjuur, Uud, whereas its concentration ranged between 16.13-57.31% in the extract from Lake Darday, Gurvan nuur, Zegstei, and Bus (Table 3).

Table 2.

The concentration and elemental composition of DOM and IOM

Lake	DOM, mg/g peloid	IOM, mg/g peloid	Elemental composition of DOM, %			
			C	H	N	Cl
Avagra toson	5.23	11.57	62.65	9.89	0.26	3.32
Bus	2.83	-	58.38	8.79	1.83	2.78
Gurvan nuur	7.73	12.93	66.05	6.25	1.57	0.07
Darday	1.43	4.84	59.66	7.05	1.83	1.18
Ikh tsaidam	2.24	1.77	63.10	8.47	0.00	0.00
Olziit	1.83	1.46	61.70	9.18	0.35	0.00
Utaat minjuur	15.51	1.22	65.18	6.55	0.00	4.05
Uud	7.11	12.86	60.57	6.89	0.52	2.58
Khotont	0.93	4.23	58.38	7.58	0.32	3.48
Khujirt	3.88	2.76	61.20	9.04	1.83	1.95
Shargiin tsagaan	0.37	1.26	66.67	8.20	0.00	2.64
Zegstei	0.77	0.84	58.48	8.77	1.58	3.58

The straight-chain  $C_{14}$ - $C_{26}$  alkanes were distributed in most DOM from peloids, but the predominance of even- or odd carbon number hydrocarbons was not observed. The sedimentary odd carbon number n-alkanes with short chains indicated algal input, while long chain alkanes represented contributions from terrestrial plants (Eglinton and Hamilton). Only one sample from Zegstei contained elevated levels of long chain alkanes  $C_{29}$ - $C_{43}$  appears 9.5%. Alkenes and monocyclic hydrocarbons (0.3-7.4%) were found in several peloids. Polycyclic aromatic hydrocarbons, which originated from anthropogenic sources, were not observed. In peloids from Lake Khujirt, Bus and Gurvan nuur the concentration of carboxylic acid varied 1.09%, 7.47, and 14.46%, respectively, while their esters ranged from 9.55-26.09% in DOM from Lake Zegstei, Khotont, and Gurvan nuur (Table 3).

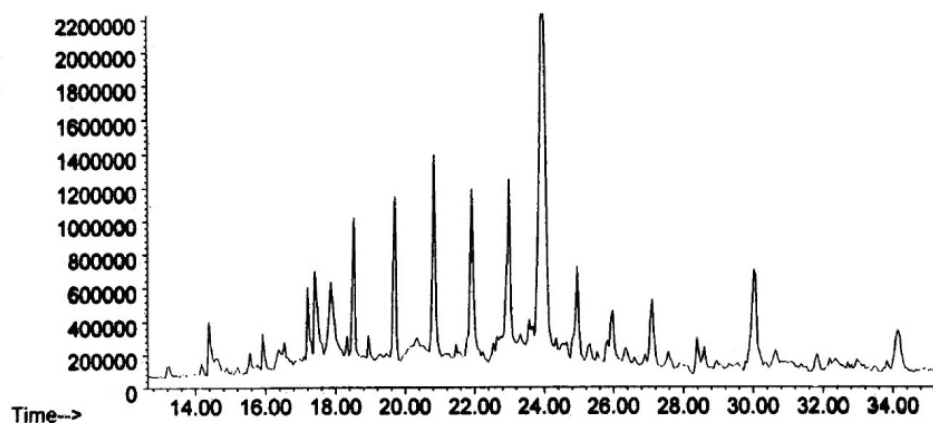


Fig.1. Mass chromatogram of DOM isolated from peloid in Lake Avarga toson

Saturated and unsaturated hydrocarbons were abundant in insoluble organic matter (IOM) of peloids from Lake Darday, Zegstei, Utaat minjuur, and Ulziit (18.99%, 28.76%, 74.8% and 76.01%, respectively). As shown in Table 3, IOM extracts contain carboxylic acids 1.62-29.25% (except Lake Uud and Ulziit), and their esters 2.55-8.69%. Silicon organic compound (hexaethylcyclotrisiloxane; tetra ethyl silan, Ethyleneglycolbis(triethylsilyl) ether; 1'-O-hexanoylsucrose) was identified in IOM from Lake Khotont, Dornod province. Organic silicon is an active component that participates, for instance, in the formulation of some antihomotoxic homeopathic medicines (Gomes et al., 2007). Therefore, biogenic silica that originates from the production of dissolved silica was quantified 0.62 % (Si) in Khotont peloid (see Table 1).

Table 3.

Lake	The chemical composition of DOM and IOM of peloids in Mongolia						Heteroatom compounds
	The content of compounds in total organic extract, % (in the dry mass of extract)						
	The hydrocarbons		The oxygen organic compounds				
Organic matter	$C_n H_{2n+2}$ (n)	$C_n H_{2n}$ (n)	RC(O)OR <sup>1</sup> (R, R')	1,2- $C_6 H_4$ (COOR) COOR <sup>1</sup> (R, R')	ROH		
Araga toson	DOM	0.52 (11-15)	-	-	1.5 (n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> ) 1.7 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> ) 94.8 (i-C <sub>8</sub> H <sub>17</sub> ; i-C <sub>8</sub> H <sub>17</sub> )	1.3	0.2
	IOM	1.63 (18-20) 1.5 (32-36) 2.0 (12-16) <sup>1</sup>	-	0.4 (C <sub>4</sub> H <sub>9</sub> ; H) 2.1 (C <sub>13</sub> H <sub>31</sub> ; H)	91.4 (n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> )	0.3 0.2 <sup>3</sup>	0.5
	DOM	1.1 (11) 1.3 (18) 1.2 (23)	-	-	0.5 (n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> ) 3.5 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> ) 95.1 (i-C <sub>8</sub> H <sub>17</sub> ; i-C <sub>8</sub> H <sub>17</sub> )	-	0.2
Ulaat minjur	IOM	1.7 (11-12) 9.4 (14) 22.7 (16) 6.9 (17) 15.1 (21-26) 0.7 (18) <sup>1</sup>	1.3 (13) 11.4 (14) 4.0 (16-22) 1.8 (35) 2.8 (12-18) <sup>2</sup>	1.8 (C <sub>17</sub> H <sub>35</sub> ; H) 2.6 (C <sub>17</sub> H <sub>33</sub> ; C <sub>2</sub> H <sub>5</sub> )	1.5 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> ) 3.9 (n-C <sub>11</sub> H <sub>23</sub> ; n-C <sub>11</sub> H <sub>23</sub> )	2.0 2.9 <sup>3</sup>	5.1
	IOM	5.3 (18-26) 1.0 (36) 2.3 (12-18) <sup>1</sup>	6.2 (16-22) 1.3 (29-35) 2.6 (9-26) <sup>2</sup>	6.3(C <sub>7</sub> H <sub>14</sub> -C <sub>14</sub> H <sub>30</sub> ; H) 16.1(C <sub>15</sub> H <sub>31</sub> -C <sub>17</sub> H <sub>35</sub> ; H) 0.3(C <sub>7</sub> H <sub>15</sub> (COO) <sub>2</sub> ; H <sub>2</sub> ) 6.6(C <sub>17</sub> H <sub>35</sub> ; H) 8.1(CH <sub>3</sub> -C <sub>11</sub> H <sub>23</sub> ; C <sub>4</sub> H <sub>11</sub> -C <sub>9</sub> H <sub>39</sub> ) 0.6(C <sub>7</sub> H <sub>14</sub> (COO) <sub>2</sub> ; (CH <sub>3</sub> ) <sub>2</sub> )	6.1 (n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> ) 1.8 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> ) 1.6(i-C <sub>8</sub> H <sub>17</sub> ; i-C <sub>8</sub> H <sub>17</sub> )	3.6 2.9 <sup>3</sup>	9.1



Khotont	IOM	1.4 (13-19) 0.6 (31) 0.4 (14) <sup>1</sup>	-	3.3 (C <sub>7</sub> H <sub>15</sub> ; C <sub>13</sub> H <sub>27</sub> ; H) 1.3 (C <sub>5</sub> H <sub>17</sub> ; C <sub>3</sub> H <sub>7</sub> ) 0.8 (C <sub>7</sub> H <sub>15</sub> ; C <sub>2</sub> H <sub>5</sub> ) 1.0 (C <sub>7</sub> H <sub>14</sub> ; (COO) <sub>2</sub> ; (C <sub>4</sub> H <sub>11</sub> ) <sub>2</sub> )	16.7 (n-C <sub>4</sub> H <sub>10</sub> ; n-C <sub>4</sub> H <sub>9</sub> ) 0.4 (i-C <sub>4</sub> H <sub>9</sub> ; i-C <sub>4</sub> H <sub>9</sub> ) 2.3 (n-C <sub>8</sub> H <sub>17</sub> ; i-C <sub>4</sub> H <sub>9</sub> )	0.6	8.7 39.6 <sup>4</sup>
Gurvan nuur	DOM	7.6 (14-18) 6.7(22) 4.6(25)	7.4(19) <sup>2</sup>	1.7 (C <sub>15</sub> ; C <sub>31</sub> ; H) 3.8 (C <sub>17</sub> H <sub>35</sub> ; C <sub>14</sub> H <sub>31</sub> ; H) 2.6 (C <sub>17</sub> H <sub>35</sub> ; C <sub>3</sub> H <sub>5</sub> ) 1.7 (CH <sub>3</sub> ; C <sub>11</sub> ; H) 8.9 (CH <sub>3</sub> ; C <sub>17</sub> H <sub>35</sub> )	4.7(n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> ) 2.8 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> )	11.9 2.0 <sup>5</sup>	3.35
Khujirt	DOM	8.2(12-16) 10.2 (18-27)	0.3 (13) <sup>2</sup>	0.5 (C <sub>17</sub> H <sub>35</sub> ; H) 0.6 (C <sub>17</sub> H <sub>35</sub> ; H) 0.4 (C <sub>31</sub> ; C <sub>63</sub> ; CH <sub>3</sub> )	7.7 (n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> ) 1.0 (n-C <sub>6</sub> H <sub>13</sub> ; n-C <sub>6</sub> H <sub>13</sub> ) 67.9 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> )	1.1	-
	IOM	0.5(14-15) 0.4 (16-23)	-	0.5 (C <sub>17</sub> H <sub>35</sub> ; H) 0.6 (C <sub>17</sub> H <sub>35</sub> ; H) 0.4 (C <sub>31</sub> ; C <sub>63</sub> ; CH <sub>3</sub> )	1.5 (C <sub>2</sub> H <sub>6</sub> ; C <sub>2</sub> H <sub>6</sub> ) 19.5 (n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> ) 2.6 (n-C <sub>6</sub> H <sub>13</sub> ; n-C <sub>6</sub> H <sub>13</sub> ) 62.9 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> )	1.6 <sup>5</sup>	-
Zegstei	DOM	1.4 (14-18) 9.5 (29-43) 5.2 (6-12) <sup>1</sup> 0.8(22) <sup>1</sup>		26.1 (C <sub>15</sub> H <sub>31</sub> ; C <sub>2</sub> H <sub>6</sub> )	3.8 (H; cyc-C <sub>8</sub> H <sub>11</sub> ) 16.3 (C <sub>2</sub> H <sub>6</sub> ; C <sub>2</sub> H <sub>6</sub> ) 13.4 (n-C <sub>4</sub> H <sub>9</sub> ; n-C <sub>4</sub> H <sub>9</sub> )	5.1	4.5
Bus	DOM	27.3(10-13) 8.7 (14) 2.6 (19) 11.4 (10) <sup>1</sup>	7.4 (12)	7.5 (C <sub>17</sub> H <sub>35</sub> ; H)	6.6 (i-C <sub>4</sub> H <sub>9</sub> ; i-C <sub>4</sub> H <sub>9</sub> ) 8.2 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> )	12.9 7.5 <sup>5</sup>	-
Olzilt	IOM	16.1(9-15) 44.3 (16-28)	14.0 (11-14) 1.7(19) <sup>2</sup>	4.9 (C <sub>8</sub> H <sub>37</sub> ; C <sub>2</sub> H <sub>6</sub> ) 2.6 (C <sub>13</sub> H <sub>29</sub> ; C <sub>16</sub> H <sub>33</sub> ; C <sub>5</sub> H <sub>7</sub> ) 1.1 (C <sub>6</sub> H <sub>13</sub> ; C <sub>8</sub> H <sub>17</sub> )	0.7 (CH <sub>3</sub> ; CH <sub>3</sub> ) 0.9 (n-C <sub>8</sub> H <sub>17</sub> ; n-C <sub>8</sub> H <sub>17</sub> ) 6.4 (i-C <sub>9</sub> H <sub>19</sub> ; i-C <sub>9</sub> H <sub>19</sub> )	3.7	1.6

Note: 1 - halogen bearing hydrocarbons; 2-cyclic hydrocarbons; 3-aldehyde; 4-siloxane; 5-ketone

Insignificant amounts of alcohol, aldehyde, ketones and heteroatom compounds were observed in most of DOM and IOM fractions. Elevated concentrations (totally) of alcohol, aldehyde and ketone were 13.9 and 20.4% in Gurvan nuur and Bus peloids, respectively. The distribution individual organic compounds was very complex, and no relationship was observed between DOM and IOM composition.

Dialkyl phthalates (with various alkyl substitutes) were found in both DOM and IOM fractions as shown in Table 3. The range for peloid DAP concentration was comparatively high (3.3-99.1%). There was no relationship between their abundance and concentration of TOM in peloids. Dibityl- and dioctyl phthalates were more abundant than other DAPs. A high fraction of DAPs were observed in both DOM and IOM from Avarga toson peloid (91.4% and 94.76%, respectively).

### 3.3. Lipid

Lipid concentrations were 0.1-2.2 mg/g in dry hydrosulfide peloids, but elevated concentrations were appear (2.9%) in the sapropel. The chemical composition of lipid was further studied by GC/MS. From Table 4, hydrocarbons (16.0-41.2%), carboxylic acids (0-1.9%), esters of aliphatic acids (16.7-53.3%) and steroids (9.3.6%) were dominant in lipid from the hydrosulfide peloid. n-Alkanes from C<sub>16</sub> to C<sub>25</sub> were more abundant among the lipid hydrocarbons. Alkanes were detected by GC/MS on fragment ions *m/z* 57+71+85+99+113.... The high content of n-alkanes in lipid from marine sediments indicates that their genesis correlated with seaweed. Marine organisms such as diatomic seaweeds produce n-alkanes from C<sub>15</sub> to C<sub>32</sub> (Afonina, 1998). The concentration and composition of alkanes indicate their biogenic genesis.

Ethyl esters of myristic- (0-3.6%), palmitic- (6.1-16.8%), stearic- (3.4-7.6%) and oleic (0-13%) acid were investigated in peloid lipid extract. Identified zoo- and phyto-steroids included cholestan-3-one; cholestan-3-ol and 22,23-dihydrostigmasterol. Also found ergosterol, which is used as an indicator of fungal biomass in sediments. The basic components of sapropel lipid are hydrocarbons (20.0%), carboxylic acids (9.0%) and their esters (7.7%), steroids (7.4%) and other oxygen containing compounds (18.0%).

Table 4.

The concentration of lipid and predominant compounds in the extracts from peloids

Lipid concentration in mg/g (dw)	Organic compounds	Total content of organic compounds, % in IOM	Dominant individual organic compounds, % in extract
Avarga toson 0.6	Hydrocarbons	33.7	Hexadecane 1.8; heptadecane 4.6; octadecane 2.2; nonadecane 1.8; eicosane 2.5; heneicosane 4.1; tricosane 3.3
	Esters of carboxylic acid	34.3	Ethyl ester- of myristic acid 3.6, palmitic acid 9.8, stearic acid 7.6; ethyl oleate 5.0
	Steroids	9.5	26—Nor-5-cholesten-3. Beta -25-one. Area-1.49%, 26-Homo-25-hydroxycholesterol 2.09%, Cholestan-3-one, 4.4-dimethyl-, 4.05%, Taraxerol 1.01%
Darday 0.7	Hydrocarbons	16.0	Heptadecane 1.5; nonadecane 1.1; eicosane 0.5; heneicosane 2.9; pentacosane 3.0
	Esters of carboxylic acid	53.3	Ethyl ester- of palmitic acid 16.2, stearic acid 7.5; ethyl oleate 13.2
	Steroids	9.3	Cholestane-3-one 4.0; cholestane-3-ol 1.7; 22.23-dihydro stigmasterol 3.2
Ikh Tsaidam 2.2	Hydrocarbons	41.2	Hexadecane 0.2; octadecane 0.6; nonadecane 1.3; tetracosane 0.6; pentacosane 0.9; nonacosane 7.3; hexatriacontane 10.9
	Esters of carboxylic acid	16.7	Ethyl ester- of myristic acid 0.7, palmitic acid 6.1, stearic acid 3.4, octacosanic acid 3.8
	Steroids	19.6	Cholestane-3-one 2.6; cholestane-3-ol 1.6; ergosterol 4.1; stigmastane-7-one 5.5
Gurvan nuur 28.9	Hydrocarbons	20.0	Tetradecane 2.5; 1.5.9-decatriene, 2.3.5.8-tetramethyl 3.0; hexadecane 7.6; heptadecane,2-methyl 1.7; cyclohexane,4-(4-ethyl cyclohexyl)-1-pehyl 9.4
	Carboxylic acid	9.0	Hexadecanoic acid 3.5; oleic acid 2.1; 9-octadecenoic acid 0.7; stearic acid 2.7
	Esters of carboxylic acid	7.7	11-tetradecenyl acetate 3.3; ethyl palmitate 1.1; hexadecanoic acid ethyl ester 1.4
	Steroids	7.4	Estean-3-one,7-(acexylo)2-methyl-(2alpha,3,17 beta) 2.4; pseudosolasdine diacetat 2.9; ergost-2.5-ene-3.6-dione,5.12-dihydroxy(5.alpha, 2.beta) 2.1

### 3.4. Humic acid

HA concentration varied from 11.2 to 55.9 percent of TOM in peloids. The highest content of HA (14.7%) was identified in the sapropel from Lake Gurvan nuur. HA concentration (2%) in the peloids from Lake Avarga toson, Bus and Khujirt was higher than other hydrosulfide peloids.

Further study was focused on the sapropel HA. The elemental composition of isolat-

ed humic acid was investigated in order to obtain general information about the sapropel HA molecular structure (Table 5). The sapropel HA from Lake Gurvan nuur had lower atomic ratio C/H (7.58) and is more aliphatic in nature than coal HA. The C/N ratio of the sapropel was 8.28.

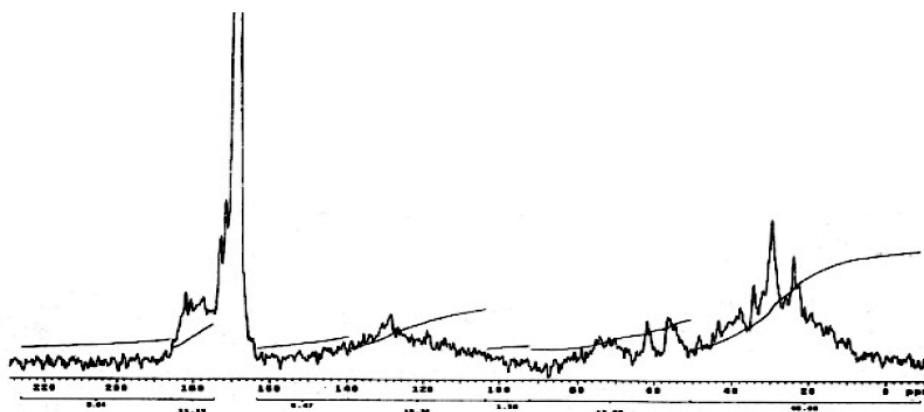
Table 5.

The elemental composition of humic acid from the sapropel

Content of elements, % of HA					Ash, %	C/H	C/N
C	H	S	N	Cl			
49.27	6.50	1.45	5.95	1.32	6.60	7.58	8.28

HA chemical properties were examined by IR and  $^{13}\text{C}$  NMR spectroscopy. In the IR spectrum of sapropel HA, a broad intense band registered at  $3440\text{ cm}^{-1}$  was assigned to OH and NH groups. The C-H stretch of aromatic ring or alkene group appears from  $3040\text{--}3100\text{ cm}^{-1}$ . The intense bands at  $2921$  and  $2954\text{ cm}^{-1}$  were assigned to the C-H stretch of methyl- and methylene groups. The bands at  $1720$ ,  $1682$  and  $1634\text{ cm}^{-1}$  were assigned to C=O stretch of carboxyl groups, and  $1540$  and  $1506\text{ cm}^{-1}$  bands due to C=C stretch in condensed aromatic systems, respectively. The  $799$  and  $751\text{ cm}^{-1}$  bands were assigned to aromatic compounds with aliphatic side assistants.

$^{13}\text{C}$  NMR spectrum is shown in Fig.2; a carbon atom (3.84%) for the carbonyl group assigned to  $226$  and  $186\text{ ppm}$ , and the signals at  $186\text{--}175\text{ ppm}$  corresponded to the carbon atom (11.19%) of carboxyl, ester, and amide.

Fig.2.  $^{13}\text{C}$  NMR spectrum of humic acid from the sapropel in dimethyl sulfoxide

The chemical shifts at  $92\text{--}50\text{ ppm}$  relate to the carbon atoms (13.88%), which are found in methoxyl, alcohol, and ether groups. The integrated area of above mentioned peaks showed that sapropel HA has a more functional groups than soil and lignite HA

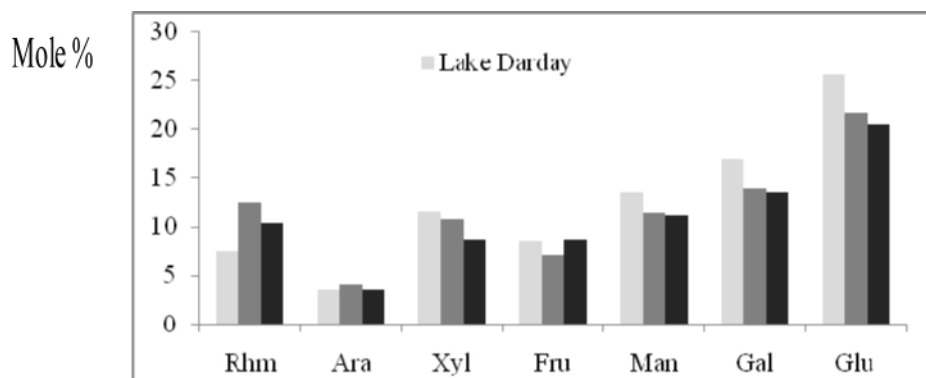
(data reported by Drosos et al., 2009). The signals at 162-140 ppm, due to aromatic carbon (5.47%) linked to the oxygen atom, at 140-106 ppm, due to aromatic carbon (18.38%) attached to carbon or hydrogen atoms, and the signals at 0-50 ppm due to a carbon (45.66%) in alkyl groups. The aromaticity of HA was calculated by expressing the level of aromatic carbon as a percentage of total contents of aliphatic and aromatic carbon atoms (28.62%), which resembled the value for HAs from river and lake sediments (Mengchang et al., 2008).

### 3.5. Carbohydrate

Carbohydrates account for a substantial amount of the dissolved and particulate organic carbon in the sediments of marine environments. Carbohydrates were isolated in peloids from Lake Darday, Ikh tsaidam, Utaat minjuur, Uud, Khujirt, and Gurvan nuur, and the concentrations were largely varied (0.02-1.60 mg/g dry hydrosulfide peloid and 4.80 mg/g dry sapropel).

IR spectrum of carbohydrates from peloid showed a broad band at 3600-3280  $\text{cm}^{-1}$  which was assigned to -OH group. The O-H stretch of the unassociated hydroxyl group in alcohols appears as a narrow band at 3670-3580  $\text{cm}^{-1}$ . The 2924  $\text{cm}^{-1}$  and 2855  $\text{cm}^{-1}$  sharp and intense bands were assigned to valence vibrations due to  $\text{CH}_2$  group. The carbonyl stretch  $\text{C}=\text{O}$  appears as an intense bands at 1680-1620 and 1590  $\text{cm}^{-1}$ , also the C-O-C stretch in the region the 1090-1050  $\text{cm}^{-1}$ .

Monosaccharide composition was studied by gas chromatography. Its compositions were not largely varied in the hydrosulfide sticky muds from Lake Darday, Ikh tsaidam and Uud (Fig 3).



**Fig 3.** Monosaccharide composition of peloids from Lake Darday, Uud and Ikh tsaidam. (Rhm, rhamnose; Ara, arabinose; Xyl, xylose; Fru, fructose; Man, mannose; Gal, galactose; and Glu, glucose)

Glucose, which is present at higher levels in vascular plants, was the most abundant monosaccharide in peloid carbohydrate extract (20.48-25.52 mol%). Galactose, xylose

and mannose contents were 13.50-16.91mol%, 8.57-11.54mol% and 11.07-13.55mol%; respectively. In order to verify the reliability of our data, we compared our results with values reported for marine and estuarine sediments. The concentration of total uronic acids varied between 13.12-24.07 mol%, and those are carboxylated acidic of polysaccharides.

Free and associated carbohydrates were isolated from Gurvan nuur sapropel. Their contents were 0.27%, 0.21%, respectively. The chemical nature of the sapropel carbohydrate was studied by the elemental analysis and molecular weight distribution. The dissoluble carbohydrate consists of 39.8% C, 4.9% H and 3.4% N, insoluble carbohydrate 37.3% C, 4.9% H and 5.3% N. These results showed that these fractions may contain protein. Protein was identified in both free (18.3%) and associated (12.2%) carbohydrate fractions by analysis.

#### 4. Discussion

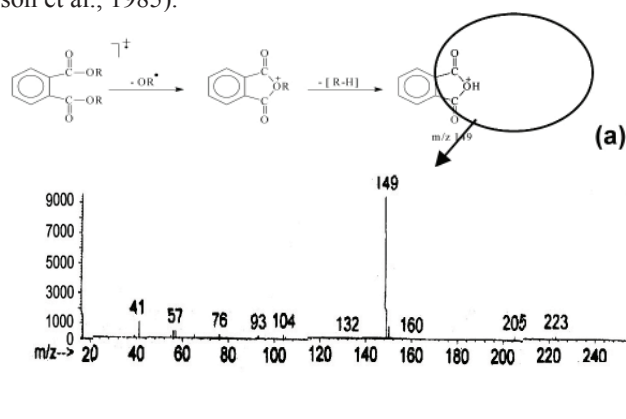
Peloids were classified according to their physicochemical characteristics including peloid color, moisture content, dissoluble sulfides and total organic matters concentration, as well as material properties related to therapeutic application (such as particles with diameter more than 0.25 mm and elasticity). The analyzed peloids have the smell of hydrogen sulfide, they are dark gray or black color, and possess elastic and adhesive characteristics (the latter assessed by touch). Moisture content, concentration of TOM, and hydrogen sulfide indicated the peloids from 11 lakes belonged to the continental hydrosulfide sticky peloids. The hydrosulfide sticky peloids from Lake Avraga toson, Bus, Utaat minjuur, Uud and Khujirt are rich in organic matter (3.7-5.4%), compared to others from the same class of peloids. In general, hydrosulfide sticky peloids formed in the mineralized water that is rich in sulfate. The increase in the availability of reactive organic matter promotes H<sub>2</sub>S formation through anoxic bacterial reduction of salt water sulfate (Allison et al., 1991). Those two processes, including oxidation of organic matter and reduction of sulfate, are linked through the microbial ecosystem. Likewise, the level of H<sub>2</sub>S in peloids Bus and Uud was slightly higher than the level for continental hydrosulfide peloids (reported data by Shinkarenko and Milenina., 1981). This was likely due to their high organic content.

The sapropel from Lake Gurvan nuur in Khentii province is suggested for healing procedure of children and the elderly due to their low mineralization and high concentration of total organic matter.

A certain part of the sediment organic carbon is loosely or tightly associated with mineral particles or held together by interaction between organic molecules. Therefore, organic content may be associated with dissoluble and/or insoluble aggregates. The compositions of isolated DOM and IOM extracts were compared using GC/MS data. Major constituents were identified as hydrocarbons, carboxylic acids, aliphatic and aromatic acid esters. There were distributed saturated and unsaturated hydrocarbons with C<sub>12</sub>-C<sub>36</sub> carbon atom. The distribution of carboxylic acids in DOM and IOM fractions is character-

ized by the predominance of the odd carbon numbered compounds (maximum at  $C_{15}$  and  $C_{17}$ ), which are considered acids produced by bacterial activities in the surface sediments (Ficken et al., 2000).

DAP concentrations in dissoluble and insoluble organic matter of peloids from Lake Avarga toson, Khujirt, Zegstei and Utaat minjuur were high. All DAPs in the ion chromatogram were dominated by peak with  $m/z$  149, which was due to the  $C_6H_4(C=O)_2O^+H$  ion. The mechanism of formation of fragment ion ( $m/z$  149) has been shown by the scheme in Fig.4 (Vulfson et al., 1985).



**Fig.4.** (a)-The mechanism of formation of  $C_6H_4(C=O)_2O^+H$  fragment ion;  
(b)-mass spectrogram of bis(2-ethylhexyl)phthalate with dominated peak  $m/z=149$

DAFs are used by chemical and polymeric industries as a plasticizer, therefore, DAPs in the environment are associated with anthropogenic sources (Afonina, 1998). However, the studied lakes are located far away from industrial sources and developed areas, and are not polluted according to Mongolian national tradition. Hence phthalates in organic extract from Mongolian peloids may not be from industrial products or waste.

A number of references specify that DAP is found in many plants. Recently, bis(2-ethylhexyl) phthalate was found in an extract from flax cannabacea (Jamyansan, et al., 2003), o-phthalic acid and phthalates were found in greens, poppy-seed, and in the oil fraction from roots *Levisticum officinalis koch* (Giam et al., 1984). DAP from peloids in Mongolia probably derived from decayed remnants of plants. Higher concentration of DAPs are not very- toxic, cancerogenic or irritating to the skin (European Chemical Industry Ecology and Toxicology Centre, 1985). As a plasticizer, DAPs can be result in giving peloid's an elastic and sticky nature.

Lipid fraction isolated from geological sediments contains a broad group of naturally-occurring molecules, which includes hydrocarbons, fatty acids and their esters, steroids, inorganic sulfur and others (Degens., 1967). Lipids penetrate through the skin more easily than water solution due to their oil solubility, and are considered anti-inflammatory (Tolomio et al., 1999; Bruno et al., 2005).

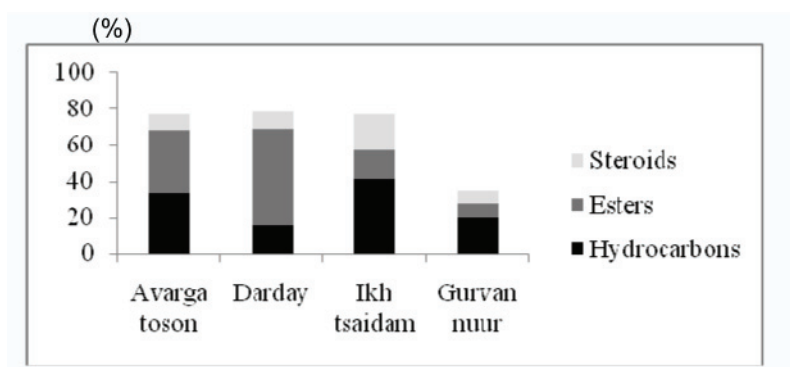


Fig.5. The predominant groups in lipid extract

The n-alkanes with carbon atom  $C_{16}$  to  $C_{25}$ , esters of saturated and unsaturated fatty acids with even carbon number  $C_{14}$ ,  $C_{16}$ ,  $C_{18}$  and  $C_{20}$ , and cholestan-3-one; cholestan-3-ol and 22,23-dihydrostigmasterol and ergosterol were abundant in most lipid extract from peloids. Lipids from the hydrosulfide peloids contain more fatty esters and steroids than the sapropel (Figure 5).

Humic substances are not found in the tissue of living plants and animals, but they formed by secondary synthesis of microbially decomposed products from the remnant of plants and animals (Manskaya and Drozdova, 1964). Generally the microbial decomposition process is more developed in sapropel compared to hydrosulfide sticky peloids. The sapropel HA from Lake Gurvan nuur ( $C/H=7.58$ ) is more aliphatic than coal HA, which was also reported by Mengchang et al., (2008). The C/N ratio of the sapropel was 8.28, indicating that aquatic plants might be the dominant contributors to these humic substances (Meyers and Ishiwatari, 1993). Characterization of HA demonstrated that peloid HA was generated from the initial biomass of reservoirs, mainly from zoo- and phytoplankton (Puntus, 1998).

According to the  $^{13}C$  NMR data the aromaticity of the sapropel HA exhibited lower (28.62%) value as HAs from river and lake sediments (Mengchang et al., 2008), while aromaticity of coal HA varied between 39.7-62.6% (Batuev et al., 2005). Data from this study indicated that sapropel HA differs due to lower molecular weight and high content of functional groups compared to other HAs. At present, HAs from sapropel are extensively used in manufacturing of cosmetic products.

The carbohydrates in peloids are the nourish, which enable numerous microorganisms to live and occupy the mud environment. Monosaccharide composition is a useful tool for identifying the sources of carbohydrates (Cowie and Hedges, 1984; D'Souza and Bhosle, 2001). Monosaccharide compositions did not vary in the hydrosulfide sticky muds from Lake Darday, Ikh tsaidam and Uud (Fig 5). In order to verify the reliability of our data, we compared our results with those reported in literature for the marine and estuarine sediments. Monosaccharide composition and ratios in peloids were similar to



the reported data (Khodse et al., 2008); that is, monosaccharides may have been derived from a mixture of phytoplankton, marine bacteria and terrestrial plants.

The distribution and concentration of organic matters in peloids chiefly reflects the relative contribution of terrestrial and marine plant inputs and bacterial activity.

During pelotherapy, chemical components, including mineral cations, many essential elements, and organic compounds, are available to penetrate the human body across the skin by diffusion and electrophoresis.

## 5. Conclusion

The physicochemical characteristics and some organic matter of peloids from 12 lakes in Mongolia were investigated. The majority of the studied peloids from Mongolian lakes were classified as continental hydrosulfide sticky peloid. But peloid from Lake Gurnu were classified as sapropel.

A variety of analyses were used to determine the amount and type of organic matter present in peloid samples. We isolated the organic matter (dissoluble and insoluble organic matter, lipid, humic acid, and carbohydrate) from the peloids and determined their composition. There were dominated by saturated and unsaturated hydrocarbons with  $C_{14}$ - $C_{26}$  carbon atoms, aliphatic carboxylic acids and their esters, and esters of aromatic acids in dissoluble and insoluble organic matter.

Lipid extracts from peloids were dominated by n-alkanes with  $C_{16}$ - $C_{25}$ , esters of fatty acids and steroids. We conclude that lipid of hydrosulfide sticky peloid differs in high concentration of fatty esters and steroids from sapropel lipid. There was dominated hexose in carbohydrate extract from the analyzed peloid. The values of monosaccharide composition and ratios suggested they derived from a mixed source of phytoplankton, marine bacteria and terrestrial plants.  $^{13}C$  NMR results showed that sapropel HA has a low aromaticity than coal HA, and high content of reactive functional groups like soil HA.

Our results suggest that the presence of known bioactive organic compounds, such as humic acid, lipid, carbohydrate, protein, as well as hydrogen sulfide, may be responsible for the balneological value of peloids in Mongolia.

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