Turkish Journal of Earth Sciences

http://journals.tubitak.gov.tr/earth/

Research Article

Turkish J Earth Sci
(2018) 27: 191-204

doi:10.3906/yer-1712-8

Chemical composition and suitability of some Turkish thermal muds as peloids

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Received: 11.12.2017 • **Accepted/Published Online:** 06.03.2018 • **Final Version:** 17.05.2018

Abstract: Thermal muds have been used in many spas for the treatment of different diseases as well as to clean and beautify the skin and in different forms such as mud baths, masks, and cataplasms. Mineralogical and chemical compositions and the possible toxicity of the peloids were investigated and compared with some limits to determine whether they have any health benefits and potential applications for pelotherapeutic treatments. The studied peloid samples were collected from 19 spas in different parts of Turkey and they were classified as neutral to slightly alkaline, with a high electrical conductivity value that had a high chlorine content and was regarded as highly conductive. The temperature of the peloids was between 23.2 and 61.0 °C. The mineralogical composition mainly comprised smectite and illite, partially quartz and feldspar, some carbonate (calcite and dolomite), and other minerals. The most abundant clay mineral was Ca-montmorillonite. The major and trace element contents of some of the peloids were similar to each other, while the contents of some toxic elements showed a clear variation. Toxic element contents, e.g., As, Cd, Hg, Pb, and Sb, of the peloids were higher or lower than the commercial herbalist clay, pharmaceutical clay, natural clay, average clay, and Canadian Natural Health Products Guide. The toxicity of some hazardous elements was compared, especially that of the pharmaceutical clay, and evaluated together with other parameters. Toxic elements were higher than in the pharmaceutical clay in most of the peloids.

Key words: Chemistry, hazardous element, peloid, therapy, toxicity, Turkey

1. Introduction

The studied peloids have been used in mud baths and cataplasms or for the treatment of muscle-bone or skin health problems and relaxation activities in spas in Turkey. Thermal muds are mainly taken from alluvial soils sourced from the host rocks in the areas surrounding the spas and are used after maturation with thermal water to obtain a cream-like mixture with physicochemical properties appropriate for application to the skin. Thermal, physical, and physicochemical properties of the peloids have been investigated and some of them have been determined to be used for therapy, healing, or cosmetics (Çelik Karakaya et al., 2016, 2017b). About 20 trace elements that are found in the peloids are considered essential or probably essential (Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, W, Mo, Si, Se, F, I, As, Br, and Sn; Lindh, 2005) for humans. Additionally, some of the trace elements, e.g., As, Be, Bi, Cd, Co, Cu, Hg, Ni, Pb, Sb, Se, Sn, Te, Tl, and Zn, are considered toxic or relatively toxic. The chemical and toxic element composition of the peloids have been examined by some researchers (Gomes and Silva, 2007; López-Galindo et al., 2007; Tateo and Summa, 2007; Tateo et al., 2009; Carretero et al., 2010). Some essential elements, e.g., Cu, Co, Fe, Mn, or Zn, may be dangerous for humans and can cause some diseases (Rovira et al., 2015, and references therein). Adamis and Williams (2005) indicated that for clays used for therapeutic and cosmetic purposes, not only the total toxic element content but also the mobility, bioavailability, and potential mobility of the substances in the products should be taken into consideration. Toxic elements can penetrate into the human body, mainly by ingestion and inhalation, and also by absorption through the skin from soils or resuspended particles of powder (Rovira et al., 2015, and references therein). It has been determined that some topically applied substances may penetrate into or through human skin and produce human systemic exposure (Bocca et al., 2014, and reference therein). Exposure to toxic elements can also cause some serious health problems, e.g., allergic dermatitis, hyperpigmentation, hyperkeratosis, acne, and hair and nail problems (Adriano, 2001, and reference therein; Afridi et al., 2006), but the accumulation of toxic elements and the collective effects of them were not taken into consideration in these research works. The absorption or penetration of the element through the skin, nails, and hair depends on several parameters, e.g., peloid and skin temperature, duration and frequency of the peloid therapy, skin integrity, cation exchange capacity, concentration of toxic elements, and dimensions of the skin area that the

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peloid is applied to. In addition, several metallic ions are found in the environment in different forms, and the toxicity of heavy metals is strongly dependent on their chemical form (Craig, 1986). Changes in the degree of the oxidation state of an element also have an important effect on the degree of bioavailability and toxicity (Stoeppler, 1992; Jain and Ali, 2000). The toxicity of arsenic is closely related to the oxidation state and the solubility of the element, so these properties should be identified before the investigation of the element's toxicity. The lack of some elements, e.g., Fe and Cu, may also cause some skin diseases, e.g., erythroderma, exfoliative dermatitis, psoriasis, eczema (Afridi et al., 2006, and references therein), and other disorders, and zinc is used in the treatment of a range of skin diseases, including acne, boils, eczema, bedsores, general dermatitis, wound healing, herpes simplex, and skin ulcers (Afridi et al., 2006).

The cation exchange capacity of clay minerals, especially montmorillonite, saponite, and sepiolite, which is a major constituent of peloids, is rather high when compared to other components, e.g., kaolinite and illite. In a common peloid therapy application, people have peloids systematically applied twice a day for about 15 days and about 20 min. The toxic elements may potentially cause systemic toxicity in the penetration through the skin during the peloid therapy. Though the toxic metals after their absorption via the skin may not cause direct health problems, their cumulative effect due to repeated application of peloids should be considered.

To date, there is no standard for the chemical composition of peloids in terms of their suitability for therapy or associated health risks. Therefore, the chemical composition of the studied peloids was compared with commercial herbal clay (CHC), pharmaceutical clay (PC), natural clay (NC) (Mascolo et al., 1999), average clay (AVC) (Turekian and Wedephol, 1961), and the Canadian Natural Health Products Guide (NHPG) (Sánchez-Espejo et al., 2014).

This study aims 1) to determine the geochemical composition of the peloids from selected spas, 2) to define their possible toxicity and health risk, 3) to recommend the suitability of Turkish peloids for therapies, and 4) to explain the relation of toxicity with chemical form, mobility, and solubility of hazardous elements.

2. Geology

Paleozoic, Mesozoic, and Cenozoic rocks are cropped in the spa areas where samples P-1 and P-20 were taken. The rocks are formed from metamorphic, sedimentary, and volcanic rocks. Quaternary units cover all of the units discordantly. The metamorphic rocks are composed of quartz, sericite schist, albite, quartzite, calc-schist, phyllite, and metabasalt. Paleozoic and Mesozoic units are composed of quartzite, schist, sandstone, siltstone, shale, dolomite, and limestone. Cenozoic units are formed from marly limestone, conglomerate, andesitic lavas, trachyandesitic lavas, basaltic lavas, conglomerate, sandstone, siltstone and shale pyroclastics, alluvium, and travertine. Alluvium overlies older units, composed of uncemented clay, sand, silt, and gravel levels (Davraz et al., 2016).

Peloid samples P-2 through P-6 were taken from the alluvium that overlies all of the units. Miocene andesitic volcanics overlie Pliocene pyroclastic ignimbrite and felsic pyroclastics, and Quaternary alluvium covers the abovementioned units and the thermal waters observed in the alluvium originally come from joints in the andesite (Özen et al., 2005). Lithological units consist of sedimentary and metamorphic rocks, their ages ranging from Paleozoic to Quaternary in the Denizli region (Figure 1). The basement rocks are composed of gneiss, schist, and marble mélange. These rocks are overlain by continental and lacustrine Tertiary sediments formed from gravel, graveled mudstone, graveled sandstone, sandstone, limestone, marls, siltstones, and travertine. The Quaternary is characterized by terrace deposits, alluvium, slope debris, alluvial fans, and travertine (Özler, 2000). The P-7 and P-8 peloid samples were taken from the southwestern part of Turkey (Figure 1). The Upper Cretaceous carbonates are basement rocks in the region. The Lower Cretaceous peridotites are overlain by the rock units and alluvium covers all of the rocks (Avşar et al., 2017). The lithologic units exposed at P-9 and the immediate area consist of Devonian to Upper Triassic sedimentary (sandstone and limestone) and volcanic rocks and are covered partially by Mesozoic limestones and mostly by Neogene andesitic volcanics and terrestrial rocks (marl, conglomerate, sandstone, and claystone). The basement rocks in the spa region from which peloid P-10 was taken are composed of Paleozoic metamorphics (schists, gneisses, amphibolites, metadunites, and marbles) and Mesozoic spilitic basalts, radiolarites, and detrital sediments, which cover the basement rocks, and they are overlain by the sandy limestones. These rocks are intruded by the granodiorites and Plio-Quaternary sediments are the youngest units in the field (Avşar et al., 2013). Peloids P-11 and P-12 are formed from the units. Paleozoic to Early Mesozoic metamorphic rocks, e.g., gneiss, schist, marble, and ophiolites, and Late Eocene to Middle Miocene basaltic, andesitic, dacitic, and rhyolitic lavas and pyroclastic rocks are overlain by Upper Miocene to Pliocene lacustrine and fluvial deposits (Gemici and Tarcan, 2002; Mutlu, 2007). The samples numbered P-13 to P-15 have been used as peloids, which were taken from the deposits. The host rocks of sample P-16 formed from Paleozoic to Mesozoic metamorphics (marbles, slates, and schists), Miocene to

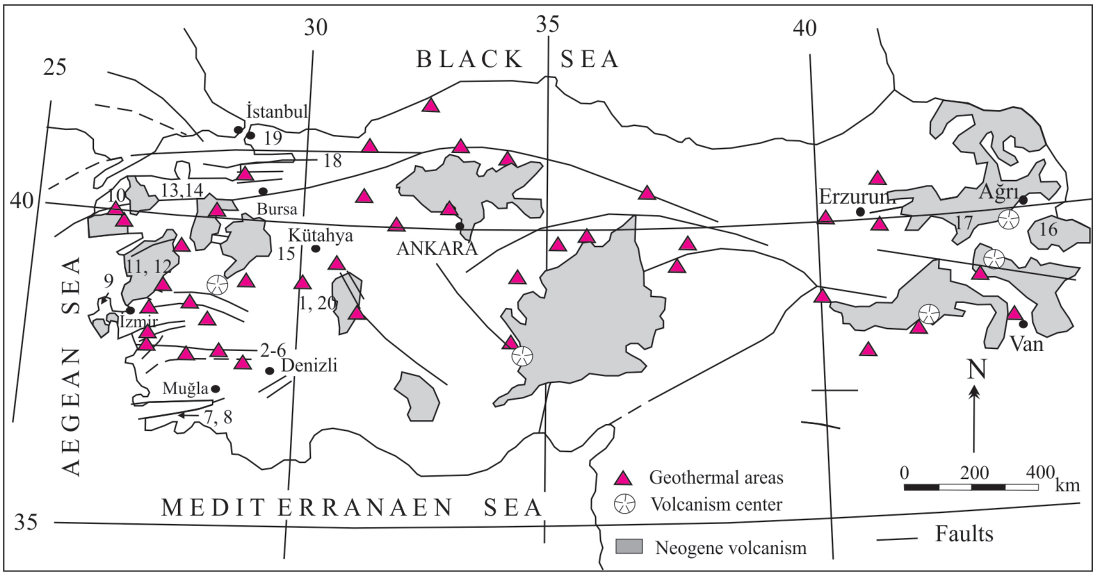

Figure 1. Location of the peloid samples and main tectonic lineaments, volcanic centers, and geothermal areas of Turkey (simplified from Şimşek, 2015).

Pliocene sedimentary rocks (detrital and carbonate), and Pliocene-Quaternary volcanic and volcanoclastic rocks (Pasvanoğlu and Güler, 2010). The Upper Miocene units formed from basaltic and andesitic lavas and volcanoclastic rocks are the oldest units and are overlain unconformably by the Pliocene sediments composed of tuffite, sandstone, shale-marl, and claystone. The Quaternary units that are the host rocks of P-17 formed from alluvium deposits, consisting of gravel, sand, silt, and clay particles (Kalkan et al., 2012, and references therein). Peloid sample P-18 formed from Eocene sandstone, siltstone, and mudstones (Saner, 1978). Sample P-19 was prepared from magnesite-rich materials by the spa.

3. Materials and methods

Peloid samples were collected from 19 Turkish spas in different parts of Turkey (Figure 1). Some parameters such as pH, electrical conductivity, and temperature of the peloids were measured on-site using a portable water quality meter (WTW 340i) (Table 1). The temperature (T, °C), electrical conductivity (EC, µS/cm), and pH were measured at an accuracy of 0.01. The pH meter was calibrated using pH 2, 4, and 7 buffer solutions, and EC was calibrated using a 0.01 mol/L KCl conductivity standard (1278 µS/cm at 20 °C and 1413 µS/cm at 25 °C). Samples were collected from different spa centers and ground gently for 5 min in a porcelain ball mill prior to chemical analysis and X-ray diffraction (XRD) analysis. The total of the major oxides and the minor, rare-earth, and refractory elements of the peloid samples was determined by ACME Laboratories (Vancouver, BC, Canada) using inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) (Spectro ICP-OES). Samples (0.1 g) were fused with Li metaborate/tetraborate (1 g) and digested with nitric acid. Loss on ignition (LOI) was determined as the weight difference after ignition at 1000 °C. The total organic carbon (TOC) and sulfur concentrations were also measured by ACME Laboratories (LECO CS230). In addition, a separate portion of 0.5 g of each sample was digested in aqua regia and analyzed by ICP-MS to determine the precious- and base-metal contents (e.g., Al, Fe, Ti, Co, Cd, Zr, Ga, and Nb).

Mineralogical analyses of the samples were performed on randomly oriented samples (total fraction) and on the clay fraction (<2 µm) using XRD (Rigaku D/MAX 2200 PC, CuKα radiation with tube voltage and current of 40 kV and 40 mA, respectively) with a scanning speed of 2°/min from 2° to 70° 2θ at Hacettepe University (Ankara). The powder samples were placed in a beaker, covered with distilled water, and immersed in an ultrasonic bath. Also, before obtaining the clay-size fraction, carbonate-rich and marl samples were decomposed in dilute HCl acid (5% HCl) at 30 °C (Jackson, 1975). The acid was added slowly to the sample beaker until the reaction stopped. Then the sample was washed several times with distilled water and transferred to a measuring cylinder; 500 mL of deionized water was added to the sample. The clay fraction of <2 µm was obtained by gravitational sedimentation of the purified samples. This clay fraction was then separated by centrifugation from the water. After removing nonsilicate minerals from the clay-sized fraction, three specimens for XRD analysis were prepared for each sample by

Table 1. Physical properties and types of the peloid samples.

Sample Number	Peloid type	pH	EC, mS/cm	Temperature, °C
P-1/1	Mature	6.45	1.71	50.7
P-1/2	Immature	6.73	2.22	---
P-2	Mature	6.93	2.64	41.0
P-3	Immature	7.20	4.02	52.0
P-5/1	Mature	8.80	3.85	70.0
P-5/2	Mature	6.48	4.70	46.9
P-6/1	Immature	7.00	4.70	79.9
P-6/2	Mature sales product	6.57	4.19	--
P-6/3	Mature	6.70	4.36	55.0
P-7	Mature	6.80	18.7	33.9
P-8	Mature	7.70	63.0	40.0
P-9	Mature	6.90	47.0	36.2
P-10	Immature	7.03	31.04	68.0
P-11	Immature	7.00	2.62	45.0
P-12	Mature	6.86	4.10	33.2
P-13	Mature	7.70	2.84	40.0
P-14	Mature	7.43	2.61	40.2
P-15	Mature	8.33	1.15	4.11
P-16/1	Immature	7.05	4.15	42.3
P-16/2	Immature	7.15	4.52	32.0
P-16/3	Immature	7.70	3.96	49.2
P-17	Mature	6.35	1.72	22.4
P-18	Immature	6.86	0.88	36.0
P-19/1	Mature	7.14	8.60	37.0
P-20/1	Immature	7.86	1.85	--
P-20/2	Mature	7.95	1.70	65.2

sedimentation onto glass slides with air drying at 25 °C; these then subjected to 1) no further treatment, 2) ethylene glycol solvation, or 3) heating at 490 °C for 4 h. The mineral proportions of the samples were taken from Çelik Karakaya et al. (2016), and results of some samples were revised using chemical analysis as stated in the caption of Table 2a. In this method, an external standard method (Brindley, 1980) developed by Temel and Gündoğdu (1996) was used. The accuracy of the mineral abundance determinations was ±15% (Tables 2a and 2b).

4. Results

The pH of the peloids was between 6.33 and 8.35 and can be classified as neutral to slightly alkaline, and the EC of the peloids varied from 1.70 to 63 mS/cm. The temperature of the peloids showed great variations between 23.2 and 61 °C (Table 1). The wide range of variation of the physical properties, and especially EC, of the peloids may be related to the distance from the main fault zone, penetrating depth, circulation time, and/or temperature of host rocks (Çelik Karakaya et al., 2017a). Nearly all of the spas are located roughly parallel to active fault systems and around Neogene-aged volcanic areas (Çelik Karakaya et al., 2017a) (Figure 1). The EC values of the peloids displayed a wide variation, and the highest values were measured in the matured peloids with high chlorine containing thermal waters or taken from near the seaside, which may reflect mixing with sea water or deep water circulation and partially long residence time. The highest EC was determined in peloid samples P-7, -8, -9, -10, and -19. The physical properties of the peloids closely resemble those of thermal water, which is used in the maturation process

Table 2a. Mineralogical composition (rare components were omitted) of the samples (revised from Çelik Karakaya et al., 2016).

Sample number	Mineralogy and mineral content (%)
P-1/1	Sme(60)+Cal(12)+Ms/Bt(10)+Fsp(8)+Qz(5)+Kln(3)+Dol (2)
P-1/2	Sme(65)+Cal(15)+Ms/Bt(8)+Fsp(6)+Qz(6)
P-2	Sme(55)+Cal(17)+Dol(14)+Ms/Bt(6)+Qz(4)+Kln(4)
P-3	Cal(95)+Sme(3)+Dol(2)
P-5/1	Sme(38)+Ms/Bt(30)+Cal(13)+Fsp(9)+Qz(5)+Kln(3)+Dol(1)+Gp(1)
P-5/2	Cal(34)+Ms/Bt(32)+Sme(18)+Fsp(5)+Qz(4)+Kln(4)+Dol(2)+Gp(1)
P-6/1	Sme(36)+Cal(28)+Ms/Bt(19)+Qz(7)+Dol(4)+Fsp(3)+Kln(3)
P-6/2	Sme(38)+Cal(24)+Ms/Bt(18)+Qz(9)+Dol(5)+Fsp(3)+Kln(2)
P-6/3	Sme(47)+Cal(23)+Ms/Bt(18)+Qz(4)+Dol(3)+Kln(3)+Fsp(2)
P-7	Sme(31)+Dol(18)+Cal(17)+Srp(10)+Kln(8)+Qz(7)+Py(5)+Gp(4)
P-8	Sme(42)+Srp(18)+Cal(9)+Ms/Bt(8)+Dol(6)+Kln(6)+Qz(5)+Fsp(4)+Hl(2)
P-9	Sme(66)+Hl(11)+Cal(8)+Fsp(7)+Qz(5)
P-10	Cal(60)+Hl(14)+Py(8)+Sme(6)+Hem(5)+Fsp(4)+Qz(3)
P-11	Sme(52)+Ms/Bt(20)+Fsp(9)+Qz(6)+Dol(5)+Kln(4)+Gp(3)
P-12	Sme(57)+Ms/Bt(15)+Cal(11)+Fsp(8)+Qz(4)+Kln(3)+Gp(2)
P-13	Sme(65)+Ms/Bio(8)+Fsp(8)+Qz(5)+Kln(4)+Cal(4)+Dol(2)
P-14	Sme(32)+Ms/Bt(22)+Cal(17)+Fsp(11)+Qz(7)+Kln(4)+Py(4)+Hl(2)
P-15	Sme(36)+Ms/Bt(26)+Cal(12)+Kln(10)+Dol (7)+Qz(4)+Fsp(3)+Gp(2)
P-16/1	Sme(73)+Fsp(6)+Qz(6)+Kln(4)+Gp(4)+Py(4)+Cal(3)
P-16/2	Sme(47)+Cal(37)+Fsp(6)+Qz(4)+Kln(4)+Gp(2)
P-16/3	Sme(61)+Ms/Bt(11)+Fsp(7)+Qz(6)+Kln(4)+Gp(4)+Py(4)+Cal(3)
P-17	Sme(60)+Cal(15)+Fsp(12)+Kln(4)+Qz(4)+Py(4)
P-18	Sme(42)+Cal(30)+Ms/Bt(16)+Fsp(5)+Qz(4)+Do(3)
P-19/1	Man(90)+Sep(10)
P-19/2	Man(82)+Spe(18)
P-20/1	Ms/Bt(37)+Cal(18)+Sme(7)+Fsp(26)+Qz(12)
P-20/2	Ms/Bt(38)+Cal(17)+Sme(11)+Fsp(21)+Qz(13)

Bt: Biotite, Cal: calcite, Dol: dolomite, Fsp: feldspars, Gp: gypsum, Hem: hematite, Hl: halite, Hyl: halloysite, Ilt: illite, Kln: kaolinite, Man: magnesite; Ms: muscovite, Qz: quartz, Sme: smectite, Sep: sepiolite, Srp: serpentine, Py: pyrite (abbreviations from Whitney and Evans, 2010).

Table 2b. Semiquantitative mineralogical composition of the CHC, PC, and NC (Mascolo et al., 2004).

	Qz	Cal	Fsp	Ms/Ill	Sme	Kao	Sulfides	Organic carbon
CHC	20	25	10	20	10	10		
PC	10–15	tr	5–10	tr	80–90			
NC	50	0	tr	10	10	10–15	6	13

Abbreviations are the same as in Table 2a; tr: traces.

(Çelik Karakaya et al., 2017b). Peloid materials are usually taken from the alluvial soil around the spa, which has been formed in situ or matured for 24 h with the thermal water. The main components of the peloids are formed from various clay minerals, e.g., smectite (Ca-montmorillonite), illite, kaolinite, and other silicates, and carbonate minerals (calcite, dolomite) have especially been identified via XRD (Table 2a). Halite, gypsum, serpentine, and pyrite are also determined in some peloids to a low extent (Çelik Karakaya et al., 2015, 2016).

The chemical composition of most of the peloids is similar and shows a direct relationship with the mineral composition, except in P-3, P-10, and P-19. Although the clay content of P-3, P-10, and P-19 is rather low, they are used as peloids. Therefore, these samples were not evaluated in detail. The SiO_2 of the peloids was between 29.66% and 64.45% of the bulk composition and Al_2O_3 varied from 4.07% to 18.05%, except in P-3, -10, and -19 (Table 3). Fe_2O_3 displays a nearly homogeneous content in most of the samples. SiO_2 presents a strong to medium

Table 3. Major (%) and trace (ppm) element content of peloids and some clay averages.

	SiO_2	Al_2O_3	tFe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI	Total	TOC	TOS	A	Cs	Ta	Th	U	Rb
P-1/1	45.37	14.04	5.14	1.88	11.39	1.05	3.01	0.70	0.22	0.13	16.61	99.55	5.88	0.15	0.09	20.8	1.4	29.1	7.2	1533
P-1/2	41.38	13.64	5.31	2.14	11.06	1.91	2.71	0.66	0.19	0.14	20.52	99.64	2.77	0.14	0.17	16.3	1.3	27.4	5.7	146
P-2	34.47	8.96	6.43	6.57	13.84	0.19	1.08	0.45	0.07	0.10	27.51	99.8	10.16	0.19	0.01	7.7	0.5	5.6	1.6	530
P-3	2.28	0.48	0.89	0.87	48.54	0.09	0.09	0.03	0.01	0.02	41.22	94.48	12.21	0.87	0.00	1.4	0.1	0.6	0.2	5.7
P-5/1	29.66	7.29	3.81	4.63	24.95	0.59	1.43	0.35	0.08	0.05	26.81	99.72	6.47	1.19	0.02	42.5	0.7	7.1	2.9	78
P-5/2	43.38	8.88	3.57	3.25	16.57	1.09	2.34	0.44	0.09	0.03	20.01	99.75	5.57	1.52	0.07	152.1	0.9	7.6	3.4	131
P-6	31.78	4.07	2.23	3.18	24.78	0.48	0.83	0.21	0.04	0.02	27.13	94.58	7.24	0.73	0.02	40.5	0.4	4.2	2.1	59
P-6/1	39.48	4.79	3.31	3.98	21.71	1.12	1.01	0.23	0.05	0.03	23.61	99.42	5.56	0.84	0.05	55.2	0.5	4.9	1.6	76
P-6/2	48.89	5.15	2.57	2.71	17.21	0.69	1.04	0.27	0.06	0.02	20.82	99.42	4.48	0.99	0.04	61.4	0.5	5.4	2.5	78
P-7	35.11	6.60	7.50	9.07	13.10	1.56	0.95	0.39	0.10	0.11	25.02	99.73	10.43	3.19	0.12	15.9	0.6	5	1.5	45
P-8	34.69	6.37	5.75	11.51	14.90	1.24	1.05	0.44	0.07	0.13	23.41	99.70	3.96	0.29	0.08	3.5	0.4	4.4	1.1	41
P-9	49.77	12.84	2.68	2.05	5.57	5.05	2.34	0.36	0.07	0.07	19.02	99.85	9.09	0.52	0.91	12.4	2.2	11.4	6.7	154
P-10	6.57	0.61	5.99	0.34	38.97	3.16	0.55	0.01	0.01	0.55	42.91	99.65	4.18	5.05	0.08	6.7	<0.1	0.9	0.2	32
P-11	60.67	12.64	6.25	0.91	1.88	1.66	4.79	0.63	0.24	0.05	10.01	99.71	4.81	1.64	0.88	43.8	0.9	19.6	4.9	194
P-12	62.53	9.73	2.91	1.39	6.68	1.30	2.07	0.39	0.15	0.07	12.50	99.68	4.47	0.46	0.19	121.7	0.6	11.7	1.9	166
P-13	54.95	14.95	5.92	2.87	4.30	1.47	2.50	0.74	0.16	0.11	11.83	99.76	5.27	0.04	0.34	28.5	1.2	15.8	3.6	132
P-14	41.11	8.69	3.83	1.70	19.44	1.31	1.69	0.54	0.16	0.08	21.20	99.75	6.45	1.11	0.07	21.1	0.8	10.9	2.5	81
P-15	46.73	10.33	4.04	1.75	14.77	1.13	2.24	0.54	0.13	0.28	17.81	99.74	8.06	0.82	0.08	139.5	0.9	11.1	1.8	156
P-16/1	64.45	10.43	2.83	0.65	2.72	1.11	1.74	0.49	0.08	0.02	15.30	99.79	3.35	1.61	0.41	289.1	1.3	12.6	2.3	106
P-16/2	35.86	8.92	2.03	1.41	23.79	0.36	0.87	0.41	0.08	0.02	26.02	99.71	10.35	0.94	0.02	207.7	1.1	7.8	1.8	64
P-16/3	46.15	18.05	6.53	1.42	1.59	0.61	1.31	0.53	0.12	0.04	23.31	99.63	1.19	3.39	0.38	215.3	1.3	14.6	3.5	111
P-17	41.37	9.32	5.10	1.66	17.50	1.10	1.37	0.47	0.22	0.09	21.62	99.86	5.05	0.06	0.06	3.7	0.6	6.6	1.6	57
P-18	36.02	9.01	4.99	1.95	20.87	0.90	1.41	0.59	0.11	0.08	23.91	99.82	6.41	0.25	0.04	10.2	0.7	5.8	1.3	70
P-19/1	6.61	0.98	0.52	41.01	1.79	0.25	0.12	0.06	0.05	0.01	47.93	99.25	12.21	0.07	0.14	11.7	<0.1	0.7	4.8	11
P-20/1	60.23	15.14	6.01	1.31	1.11	0.99	3.20	0.60	0.17	0.18	10.81	99.79	0.27	0.03	0.89	48.6	2.2	25.4	3.5	271
P-20/2	60.57	15.38	5.75	1.34	1.11	0.99	3.18	0.60	0.17	0.17	10.52	99.78	0.22	0.04	0.89	52.7	2.1	27.1	3.9	300
MDL	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	5.10	0.01	0.02	0.02		0.1	0.1	0.2	0.1	0.1
CHC	41.76	13.49	5.22	2.01	13.88	0.48	2.17	0.66	0.17	0.04	19.5	99.4	3.36	0.47	0.03	4.3	1.3	8.4	2.5	83
PC	47.91	12.81	3.06	2.96	1.27	0.37	0.23	0.24	0.05	0.03	30.08	99	6.11	0.04	0.29	3.3	0.9	8.8	2.1	11
NC	57.76	8.83	4.63	0.37	0.03	0.21	0.64	0.43	0.03	0.02	27.64	100.6	ng	3.05	7.00	2.3	<0.3	5.3	11	32
AVC	58.41	15.11	6.72	2.47	3.09	1.35	3.25	0.77	0.16	0.11	ng	ng	ng	0.24	0.44	5	0.2	12	3.7	140

CHC: Commercial herbalist clay, PC: pharmaceutical clay, NC: natural clay (Mascolo et al., 1999), AVC: average clay (Turekian and Wedephol, 1961), NHPG: Canadian Natural Health Products Guide (Sánchez-Espejo et al., 2014), LOI: loss on ignition, MDL: detection limit, ng: not given, tFe_2O_3: total iron, tREE: total REEs, A: Na_2O/CaO.

positive relationship with some of the main oxides, e.g., Al_2O_3, TiO_2, K_2O, Na_2O, and P_2O_5, and shows a negative correlation with CaO. This correlation indicates that the main minerals of the peloids were formed from silicate minerals while MgO and Fe_2O_3 contents are related to nonsilicate or partially iron-rich smectite minerals in the peloids. CaO and K_2O contents of the peloid and soil samples were higher while Al_2O_3, SiO_2, and partially Na_2O contents were lower than the values of the peloids in the literature (Table 3). Na_2O/CaO ratios of the samples are lower than 1.0 and they are mostly similar to that of CHC (Table 3). The total sulfur (TOS) content ranges from 0.03% to 3.39% and the TOS contents of the P-7 and P-16/3 samples are slightly over 3.0%, while the others are low.

Due to the absence of data on the levels and no guidelines or regulations of the element content, for especially toxic elements permitted in therapeutic mud, the results of the studied peloids were compared with other similar products in literature (Summa and Tateo, 1998; Mascolo et al., 1999, 2004; Rebelo et al., 2011;

Table 3. (Continued).

	Sr	Ba	Co	Cr	V	Zr	Y	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Hg	Tl	Se	tREE
P-1	1291	1333	16.5	68	97	327.7	24.8	0.3	26.3	29.7	51	37.5	75.9	0.1	0.3	0.03	0.5	<0.5	309.6
P-1/1	922	1039	15.4	68	101	285.1	21.2	0.6	32.1	40.0	58	43.2	36.1	0.2	0.3	0.01	0.5	<0.5	274.5
P-2	1722	134	39.4	410	121	87.6	16.9	0.3	31.1	8.2	47	522.1	3.6	0.2	0.1	0.03	0.2	<0.5	89.3
P-3	29832	79	1.5	1.0	48	13.7	2.4	<0.1	1.1	0.6	2	18.6	4.2	<0.1	<0.1	0.05	<0.1	<0.5	8.8
P-5/1	9082	264	14.7	205	92	72.4	14.6	0.6	15.5	11.2	33	156.4	48.0	0.1	60.9	27.87	0.2	<0.5	88.8
P-5/2	600	369	17.5	192	82	121.4	15.9	1.1	26.0	17.3	45	139.2	104.9	0.1	80.2	50.0	0.3	5.4	105.4
P-6/1	4195	124	7.6	137	65	48.4	8.0	1.0	7.2	6.1	16	67.2	83.1	<0.1	92.6	0.16	0.2	0.6	51.1
P-6/2	37665	199	25.7	383	55	63.7	10.4	2.1	11.1	8.3	24	419.7	134.9	0.1	32.4	0.1	<0.1	<0.5	61.8
P-6/3	2957	1130	11.3	389	56	84.4	10.8	2.2	12.1	8.9	22	112.7	155.9	<0.1	78.2	0.11	0.1	0.8	70.2
P-7	532	117	47.0	889	74	81.2	18.0	0.5	36.0	8.3	54	564.7	98.9	0.3	0.2	0.45	0.1	<0.5	83.3
P-8	346	159	56.1	753	84	77.6	13.2	0.2	26.7	6.4	38	659.0	12.5	<0.1	<0.1	0.02	<0.1	<0.5	76.5
P-9	263	383	8.3	68	46	127	25.9	1.4	8.7	25.7	29	18.5	4.9	0.2	0.2	0.06	0.5	<0.5	103.6
P-10	2464	273	0.4	68	32	17.6	1.9	0.2	0.9	0.9	2	<0.1	76.1	<0.1	2.8	0.01	2.2	<0.5	8.6
P-11	497	1157	53.7	68	65	210.2	21.1	0.2	120	23.7	249	48.3	341.9	1.2	73.8	>100	7.1	3.0	168.1
P-12	1358	822	7.9	68	54	83.8	14.2	0.4	13.4	15.7	75	13.4	24.4	0.1	5.0	11.51	1.0	<0.5	114.5
P-13	286	797	22.5	192	101	163.4	24.7	0.2	31.7	46.1	69	103.5	57.0	0.2	1.0	0.08	0.7	<0.5	165.7
P-14	733	649	22.3	137	59	161.6	19.5	1.1	23.5	42.8	50	80.4	74.0	0.3	1.8	0.31	5.0	<0.5	130.2
P-15	647	643	11.2	68	60	144.8	20.9	0.4	14.8	32.6	68	28.8	92.1	0.3	4.0	0.02	0.6	<0.5	133.6
P-16/1	300	576	5.5	62	59	198.1	39.2	0.4	17.4	12.6	33	17.3	51.7	<0.1	0.1	0.03	0.2	<0.5	175.4
P-16/2	965	840	5.2	68	42	136.1	15.0	0.2	11.1	12.7	35	16.6	61.1	<0.1	<0.1	0.02	0.2	<0.5	113.6
P-16/3	764	1372	15.5	137	91	243.2	17.5	0.4	19.0	19.7	55	53.3	210.5	0.4	<0.1	0.09	0.2	<0.5	177.4
P-17	415	327	15.4	164	81	122.5	14.0	0.2	29.8	7.5	35	97.9	8.1	0.2	<0.1	0.02	<0.1	<0.5	87.2
P-18	399	398	15.1	151	100	112.3	17.6	0.5	30.9	11.1	47	79.4	31.1	0.1	1.1	0.1	0.1	1.4	97.2
P-19/1	502	167	1.6	21	24	8.8	1.4	0.5	6.0	1.7	6	16.5	9.9	<0.1	<0.1	0.01	<0.1	<0.5	8.4
P-20/1	145	480	15.1	103	104	274.1	29.8	0.3	31.9	23.8	42	40.0	8.8	0.2	0.3	0.02	0.4	<0.5	226
P-20/2	162	491	17.5	110	111	303.2	35.8	0.4	32.9	26.1	44	44.5	10.4	0.3	0.3	0.01	0.5	<0.5	240.8
MDL	0.5	1.0	0.2	0.1	8.0	0.1	0.1	0.1	0.1	0.1	1.0	0.1	0.5	0.1	0.1	0.01	0.1	0.5	0.1
CHC	695	248	13.3	82	109	145	23	0.3	16.7	11.9	61	40	2.88	0.18	0.45	<0.01	<0.5	<0.2	35.1
PC	100	147	5	68	24	162	29	0.3	4.71	8.01	9	5	<0.3	0.02	0.22	<0.01	<0.5	<0.3	25.8
NC	42	75	28	96	749	75	12	2.1	154	27	58	324	140	1.3	12.3	61	7.5	20.8	24.7
AVC	300	580	19	89	130	160	26	2.6	45	20	95	68	13	0.3	1.5	400	1.0	0.6	92
NHPG	ng	1300	5.0	1100	ng	ng	ng	1.8	130	≤50	ng	60	≤8	3.0	5.0	1.0	0.8	17	ng

Mihelčić et al., 2012). Major element oxides and some of the trace elements of the studied peloids were normalized to CHC (Mascolo et al., 1999). SiO_2, Al_2O_3, Fe_2O_3, and CaO are depleted compared to CHC in nearly all samples while MgO showed a slight or clear enrichment in most of the samples (Figure 2a). Chemical analyses of the samples showed that major oxide contents of the samples are mainly similar to those of CHC and NC, and partly to PC. Cr_2O_3 content is higher than 1.0‰ in two peloids (P-7 and P-8) and may be sourced from the parent rocks (ophiolitic rocks) around the spas. Chromium, copper, molybdenum, and nickel displayed enrichment or a trend similar to CHC in nearly half of the peloid samples (Figures 2a–2d).

Cr is higher than in the PC and partially than in CHC, NC, and AVC. Significant differences were also observed in other trace element contents of the peloid samples. The Ba contents are over 1000 ppm in samples P-1/1, P-1/2, P-6/3, P-11, and P-16/3, and lower in other samples. Ba content of the PC and CHC was given as 147 ppm and 248 ppm, respectively (Mascolo et al., 1999). In this case, the Ba content was found to be above these values in 70% of the samples, but there is no information on barium toxicity or side effects.

Contents of trace elements (e.g., Cd, Co, Rb, Sb, Sr, Th, U, and Hg) were distinctively higher than in the CHC and PC and partially the NC in nearly half or most of the peloids (Table 3). The contents of Sr were generally high in CaO-rich samples, and they showed a medium positive correlation ($r = 0.65$), but P-5/1 and P-6/1, which have a similar CaO content, presented quite a different Sr content. The Sr content was obviously high in samples P-6/1 and partially so in P-3 and P-10, but lower especially in samples P-2, -7, -9, -17, -18, -19, and -20/1 than the other peloid samples. There is no relation between CaO and Sr, and the presence of 4195 ppm Sr in P-6/1 and 2983 ppm in P-3 indicates that Sr does not cooperate with Ca, with the forming of an independent Sr mineral. Rb contents were generally similar in all samples, but P-20/1 and P-20/2 display somewhat higher values than the other samples. There is a strong positive correlation ($r = 0.90$) between K_2O and Rb, indicating that Rb is associated with silicate minerals (e.g., illite/muscovite, orthoclase). The contents of Au, As, Hg, and Sb are significantly high in sample P-11. The As contents of some of the peloid samples, especially P-1/1, -5/1, -6/1, -7, -15, and -16/3, were also higher than those of the other peloid samples. The Hg contents were clearly high in P-5/1 and P-11. This high content of toxic elements is probably related to deep circulation of warm waters that are used in peloid maturation in spas. There is a positive correlation between Th and U ($r = 0.69$) and Th and K_2O ($r = 0.83$) and Al_2O_3 ($r = 0.82$) and with SiO_2 ($r = 0.73$), indicating that these elements are related to the

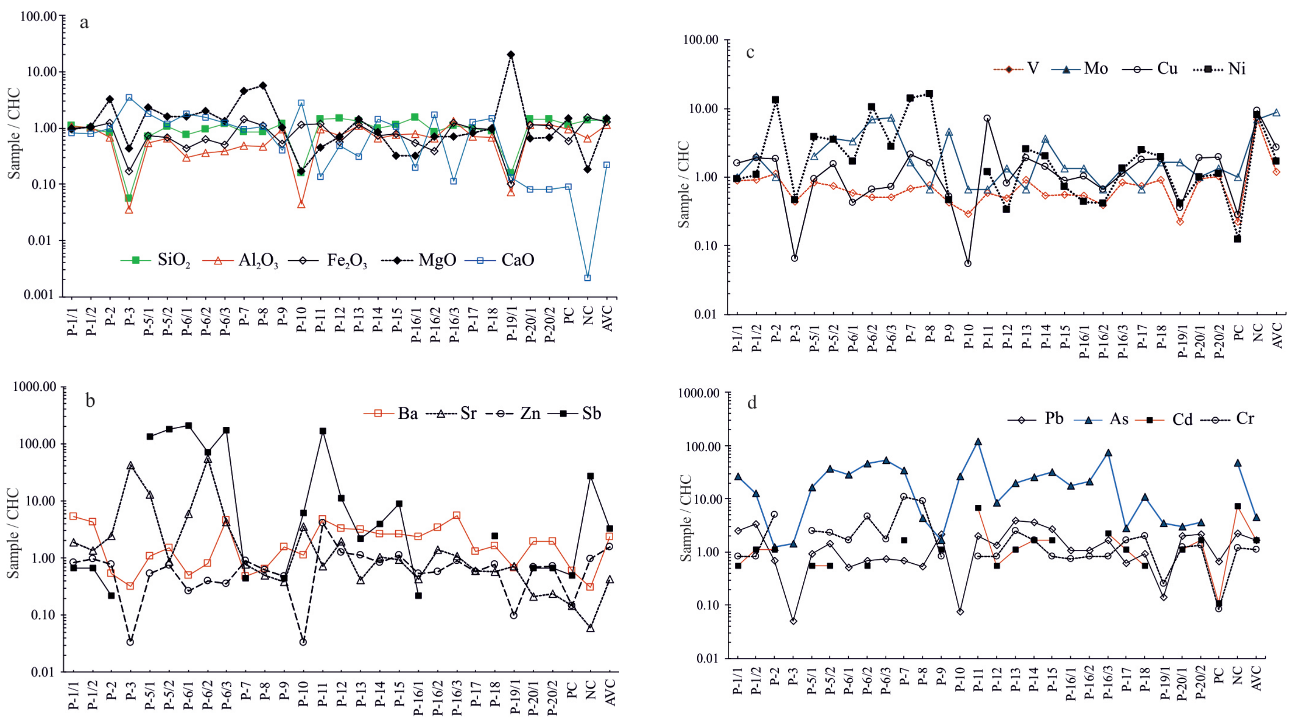

Figure 2. (a) Some CHC-normalized major element patterns of the investigated peloid samples; (b, c, d) some CHC-normalized trace element diagrams of samples. Data are from Table 3; abbreviations as in the table.

silicate minerals and especially to the abundance of clay minerals.

The toxic or hazardous element contents (As, Cu, Mo, Ni, Sb, Se, Pb, Zn, etc.) of peloids vary considerably. The contents of some of the trace elements, e.g., Ba, Cd, Cr, Cu, Mo, Pb, and Se, are below the NHPG limits while As, Co, Hg, Ni, and Sb are over the limits in some or most of the samples (Table 3). The Ni contents vary from <0.1 to 659 ppm, related to the host rock, e.g., ophiolites or basic volcanics, of alluvium. The element contents of especially samples P-2, -7, and -8 and partially of P-5/1 are higher than those of other samples (Table 3; Figures 2c and 2d). The Pb contents are especially high in P-1/1, -1/2, -13, -14, and -15 and partially so in P-20/2 samples, and they are depleted compared to CHC and somewhat similar to PC, NC, and AVC in nearly half of the peloids. The Sb content is clearly enriched one hundred times in P-5/1, -6/1, and -11 compared to CHC and depleted more so than in PC in four samples (Figures 2c and 2d). The As content is higher than in CHC and PC while it is lower than in NC and AVC in some peloids. A clear enrichment was observed in especially As (one to one hundred times) and partially in Sb, Ba, and Sr (Figures 2a–2d).

The arsenic content in most of the investigated thermal waters is 100 times higher than that of drinking water standards (WHO, 2011; Çelik Karakaya et al., 2013), as its concentration values are between 3.6 and 342 ppm. The arsenic contents of all the peloids are much higher than in both CHC and PC (Table 3). Arsenic rarely occurs in a free state; it is largely found in sulfur, oxygen, and iron compounds (Jain and Ali, 2000, and references therein). Since arsenic rarely exists in a free state in water or soil, it is thought that arsenic may be found as a compound in the studied peloids. There is no clear correlation between As and some heavy elements (Fe, Pb, Zn, Cu, Mo, and Sb) and TOS. The absence of any correlation between arsenic and TOS may indicate that no sulfur compounds have been formed. Mostly arsenate $(AsO_4)^{3-}$ and arsenite (AsO_2) compounds may occur in the peloids.

5. Discussion

The high content of clay minerals in most of the samples makes them suitable for pelotherapy because the physicochemical and rheological characteristics of the minerals improve the desired properties of the peloids. Quartz was found in nearly all of the samples in low amounts (Table 2a). Despite limited experimental data in humans, its content should be reduced since quartz is classified as a carcinogenic mineral in Group 1 by the IARC (1997), and dust of quartz or cristobalite is accepted as carcinogenic to humans (IARC, 2012). However, it was stated that crystalline silica did not show the same carcinogenic potential in all cases (Sánchez-Espejo et al., 2014). In addition, the same researchers reported that the coexistence of quartz and clay minerals prevents many of the side effects of peloid therapy. Although contents of carbonate minerals higher than 30% in some samples negatively affect the required physicochemical properties of the peloids, they can be considered as innocuous components (Sánchez-Espejo et al., 2014).

The semiquantitative mineralogical composition of the CHC is somewhat similar to those of some of the peloids while NC and mostly PC have different mineralogies than the investigated peloids (Mascolo et al., 1999) (Tables 2a and 2b). Most of the major and trace element contents of the peloids are somewhat different, commonly related to: 1) adsorption by clay minerals, 2) impurities in the structure of clay minerals, 3) possible contamination during the manufacturing or maturation (Mattioli et al., 2016), 4) outcropped rocks in the nearby area of the spas, and 5) physical and chemical properties of thermal water used for the maturation of the peloids.

Chemical analysis of the peloids demonstrated that the highest Si concentration was found in peloids P-11, -12, -16/1, -20/1, and -20/2, and partially so in P-1/1, -1/2, -5/2, -6/2, -9, -13, -15, -16/3, and -17 (Table 3). Al and K contents are high in most of the abovementioned samples in similar concentrations. Fe and Ti contents are usually associated with Fe-containing minerals, e.g., biotite, pyrite, and hematite, and partially smectite and illite, and are elevated in the same samples (Tables 2a and 3). The Ca contents of the peloids are between 1.11 and 38.97, also mainly related to the presence of carbonate minerals, e.g., calcite and dolomite, as well as Ca-smectite in the alluvium. The Si, Al, Fe, Ca, Ti, and K of clays have been reported as elements that play roles in cell renewal, invigoration and reinvigoration of tissues, removal of bacteria, and activation of blood circulation and as antiseptics (Gomes, and Silva, 2007; Favero et al., 2016).

The SiO_2, Al_2O_3, and K_2O contents of peloids P-11, -12, -16/1, and -20 are commonly high in the alluvium sourced from magmatic rocks, detrital sedimentary rocks, and metamorphic rocks (gneiss, schist, quartzites). Ca-montmorillonite (smectite) and CaO contents of the peloids are generally above 50% and 10% in most of the samples, respectively (Tables 2a and 3). Calcium availability in soil depends on the type of clay minerals, 2:1 clay minerals having relatively high Ca saturation. Smectites have a high layer charge, very fine particle size, high cation exchange capacity, and high specific surface area (Carretero et al., 2010). Montmorillonite, generally used for healing clays, belongs to the smectite group. Its structure is formed by two tetrahedral sheets and an octahedral sheet, and the ion deficiency in the sheets is compensated by interlayer exchangeable cations (Ca, Na, K) (Moore and Reynolds, 1997). Due to the specific character of their structure, the clay acts as an active sorbent. Szántó and Papp (1998) explained that Ca is provided by a topical application of Ca-bentonite and can pass the skin barrier. The authors also noted that increasing amounts of bentonite per square centimeter (to 2 g bentonite/cm^2) increased the transfer of Ca. During pelotherapeutic treatment, the loading of peloid has a high Ca-smectite thickness of 3–5 cm, which may be helpful for cases of Ca deficiency, e.g., osteoporosis (Barbieri, 1996). According to the abovementioned explanations, most of the studied peloids can be used for Ca deficiency. On the other hand, the high content of carbonate in the peloids stimulates blood circulation, especially in psoriasis, and provides optimum stratification of the epidermis (Mihelčić et al., 2012, and references therein).

The Ba content of some peloid samples is slightly higher than in CHC (Figure 2b). Considering this, Ba may not cause any skin problems and can be used in masks, baths, cures, patches, etc. (Table 3).

Sulfur is more enriched than in CHC, PC, and AVC and partially NC in some of the peloid samples (Table 3). Sulfur can penetrate the skin during therapy and cause vasodilatation in the thin veins and it has an analgesic effect on pain receptors, and sulfur-rich peloids can be recommended for acne, psoriasis, and seborrhea applications (Quintela et al., 2012). The investigated sulfur-rich peloids can thus be used for the treatment of similar skin diseases.

The presence of especially toxic elements (As, Ba, Cd, Co, Hg, Pb, Ni, Se, Sb, Te, Tl, Zn) and less hazardous elements (Li, Rb, Sr, Cr, Mo, V, Zr, REEs) are not accepted in cosmetic products and peloid therapy, and great attention should be paid to the contents of such elements (Mascolo et al., 1999; Tateo et al., 2009; Carretero et al., 2010; Rebelo et al., 2011; Sánchez-Espejo et al., 2014; Mattioli et al., 2016). In addition, Canadian food and drug guidelines declare that some heavy metal contents in cosmetic products must not be allowed to exceed Pb > 10; As, Cd, Hg > 3; and Sb > 5 ppm (Rebelo et al., 2011). Elements considered harmful to health can be found naturally in absorptive/adsorptive particles and mineralogical compositions during therapeutics (Mascolo et al., 1999; Lopez-Galindo et al., 2007).

Trace elements were divided into three groups (Rebelo et al., 2011, and references therein): 1) Cd, Pb, and As are in the first class as elements creating environmental problems that are toxic to human health and therefore should not be present (United States Pharmacopeia, 2010); b) in the second class, the toxicities of Mo, Ni, V, Cr, Cu, and Mn are lower, but their use for medical purposes should be limited; c) the third class of elements (e.g., Ba, Sr, Zn, and Sb) may be present as impurities in some cosmetic products. The studied peloids were evaluated in these three categories according to trace element contents and the elements exceeding the limit values. Ba and Se have no significant toxicological features and their risks are low, and a limit value for cosmetic products has not been proposed (Health Canada, 2009). While there is no problem with Cd from the first class of toxic elements, some of the peloids can cause toxicity due to Sb content. The elements considered as partly toxic from the second group (Cu and Mo) are above the contents of CHC and PC in some samples and V in none of the samples. A limit for nontoxic, tolerable element content was given only for Zn, but the limit was not exceeded in all samples.

The contents of the toxic or partially toxic elements (Cr, Cu, Ni, Pb, Zn, As Cd, Hg, Se, Sb, and Tl) in Morinje mud (Mihelčić et al., 2012) were given in the following ranges (ppm): Cr: 84–160, Cu: 18–48, Ni: 47–78, Pb: 9–35, Zn: 57–95, As: 12–22, Cd: 0.5–0.7, Hg: <1, Se: <1, Sb: 0.4–1.3, Tl: < 0.5. In the studied peloids, some toxic and partially toxic element contents (Cr, Cu, Ni, Pb, Zn, As Cd, Hg, Se, Sb, and Tl) are higher or lower than in Morinje mud (Table 3). Hg, As, and Sb are clearly higher than in Morinje mud (Table 3). The Cr_2O_3 content of some peloids is higher than the others and it may be sourced from ultrabasic rocks cropped out in and around the spa areas (Table 3). Mascolo et al. (1999) pointed out that high concentrations of Cd, Cu, Cr, Ni, Pb, and Zn may cause some problems for organisms. When the peloid samples are examined in this respect, it is thought that the contents of Hg, Ni, Pb, and Sb in four samples could cause some health problems, as well as arsenic.

Some hazardous element contents of the studied peloids are higher or lower than those of CHC, PC, and NHPG used in treatment (Mascolo et al., 1999). The As content exceeded the contents of CHC, PC, NC, AVC, and NHPG in all of the peloid samples while Pb exceeded that of CHC, PC, NC, and AVC in some samples (Figure 2; Table 3). Inorganic As has been classified as carcinogenic to humans (Group 1) by the IARC (1989). Arsenic can be easily solubilized in groundwaters depending on pH, redox conditions, temperature, and solution composition (Smedley and Kinniburgh, 2002). The oxidation state of As also controls the sorption behavior and subsequently the mobility in the aquatic environment (Jain and Ali, 2000). Natural dissolution of As-containing minerals existing in the aquifer, peloid-sourced rocks, or thermal waters used for peloid maturation may cause high As content. Arsenic has a distinct affinity for skin and keratinizing structures such as hair and nails, and its adverse effects can include a variety of skin eruptions, alopecia, and striation of the nails but also skin cancer (Guy et al., 1999). Pharmacopoeia impurities only refer to arsenic and lead content. According to the reports (NRC, 1999; US FDA, 2003; EPA, 2004; ATSDR, 2007), systemic dermal absorption of arsenic from soil via the skin is very low (3%). Thus, even if the arsenic content is high in nearly all samples, the toxic effect is unlikely to be harmful due to the low skin absorption. However, attention should be paid to arsenic content and its content should be lowered. Generally, most of the samples with high As content also contain high Pb; therefore, the Pb content should be taken into account in supplying new raw material. The absorption percentage also depends on the peloid application area and duration as well as temperature, pH, conductivity, etc. The mobility of all heavy metals is low at neutral to slightly alkaline pH of the peloid solution, and the solubility of Pb in soil solution was pH-dependent while the mean of 44% of the fractional sum of Cd is in exchangeable form in acid soil by enhancing its mobility (Sherene, 2010). In addition, Sherene (2010) indicated that the lower the pH value is, the more metal can be found in the solution and thus more metal is mobilized. Additionally, Razo et al. (2004) indicated that Pb mobility is low in neutral or alkaline soils due to the formation of insoluble salts, whereas, As, Cu, and Zn mobility is greater due to the relative solubility of the complexes that could form in the same soils. Besides, Cl^- can contribute in reducing heavy metal adsorption and greatly influences the mobility of metals, e.g., Cd, Fe, Ni, Pb, and Zn, by the formation of negatively charged or neutral species in the form of relatively insoluble Cl complexes in soils (Kikouama et al., 2009; Sherene, 2010). The toxic or intolerable metals will be more mobilized in EC-enriched peloids, e.g., P-7, -8, -9, and -10, and may not cause the undesirable effects of toxic elements. Absorption of Co through the skin is low (Leggett, 2008). The greater content of Co than in CHC and PC in some peloids may not cause dermatological problems (ATSDR, 2004). In addition, the allergic dermatological effects of Co will be chiefly more effective in peloids containing high levels of chlorine (Nielsen et al., 2000, 2002). The mean soil concentration of Ni is 50 ppm (Steinnes, 2009) and the NHPG limit is 60 ppm. Ni content was also greater than the limit in most of the samples (P-2, -5/1, -2, -6/2, -6/3, -7, -8, -13, and -17; Table 3). It has been stated that nickel can penetrate the skin of humans and animals (Sánchez-Espejo et al., 2014). Despite the dermal absorption of metallic nickel being fairly low, Ni-chlorate and sulfate can penetrate the skin and cause an allergic skin reaction (ATSDR, 2005; Das et al., 2008; Steinnes, 2009). The presence of Ni above the NHPG limit and the chlorine and sulfate contents of the peloids must be taken into account. Fan and Kizer (1990) indicated that skin exposure to selenium may cause severe local irritation, creating painful burning, erythema, and rarely allergic dermatitis. The Se content of the peloids was above that of CHC and PC, partially so compared to AVC, and lower than that of NC and NHPG, which may cause serious skin problems.

Despite the higher content of copper than in PC in most of the samples, it can display disinfectant activity by reducing the transmission of infectious microbial agents and preventing the growth of some microorganisms (Williams and Haydel, 2010, and references therein). It was indicated that other metallic oxides, e.g., zinc oxide, magnesium oxide, and calcium oxide, as well as titanium and silicon dioxide, have antibacterial activity with demonstrated effectiveness against *Escherichia coli* and *Staphylococcus aureus* (Sawai, 2003; Williams and Haydel, 2010, and references therein). *E. coli* was found in samples P-12, -16/1, -17, and -20/1 in terms of coliform bacteria while *S. aureus* was seen only in P-18 and -20/1 (Çelik Karakaya et al., 2016).

Considering only the toxic element contents is not enough to define the suitability of peloids in therapy. There may be some indirect effects of other chemicals, and so the nature of those effects should be investigated and interpreted in detail. Absorption of toxic elements through the skin depends on many factors, e.g., skin integrity, skin and peloid temperature, concentration and mobility of the elements in the peloids, duration and frequency of the peloid therapy, cation exchange capacity of the peloid, and dimensions of the skin area that the peloid is applied to.

6. Conclusion

The studied peloids are geomaterials with generally different mineralogical compositions and elemental contents. They have been used in therapy and partially as cosmetics despite some of their hazardous element contents. Scientific evaluation of their safety is difficult because of the lack of toxicological data on the reliability of peloids.

The suitability of some Turkish peloids for therapy, especially in terms of trace and partly major element contents, has been examined. Most of the studied samples contain Ca-montmorillonite as the main mineral phase; other clays and nonclay minerals are also present. The mineralogical and chemical composition and mainly the trace element contents of the studied peloids moderately satisfy the pharmacopeia necessities regarding As, Cr, Hg, Pb, and Sb as toxic or partially toxic elements. Additionally, when compared with PC, each of the heavy metal contents displayed greater values in nearly half of the samples, which are drastically lower than those found in CHC and the NHPG limits. Furthermore, As, C, Ni, and partially Pb presented greater values than the limits in all samples. The pH of the peloids is neutral to slightly alkaline; therefore, the solubility of toxic or partially toxic elements will be low in especially high EC-containing peloids. Also, the dermatological absorption of As and Co is low; therefore, the toxic effect of the elements may not be a serious problem. In some peloids containing Cu, Zn, Ca, Si, Ti, and Mg contents that are higher than those in PC, the development of microorganisms will be prevented due to the antibacterial effect of the elements. In order to evaluate the solubility or mobility of toxic elements, the acidity, Cl content, and reductivity of peloids should be controlled both in the maturation process and during therapy.

Acknowledgment
This study was funded by the Scientific and Technological Research Council of Turkey (TÜBİTAK 110Y033) and the Selçuk University Scientific Research Projects Support Program (BAP 11401045).

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