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Chemical, mineralogical, and physicochemical features of surface saline muds from Southwestern sub-basin of the East Vietnam Sea: Implication for new peloids

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ABSTRACT

This study presents the chemical, mineralogical and physicochemical features of 8 saline mud samples from 8 gravity cores located in the southwestern sub-basin of the East Vietnam Sea. The grain-size analysis of mud samples reveals the amount of clay and silt particles in the ranges of 65.1-89.2% and 9.5-34.2%, respectively and a very low fraction of sand. The analytical results showed that mud samples have high contents of SiO₂ (32.79-48.09%), Al₂O₃ (11.26-13.63%), CaO (3.10-13.93%), Fe₂O₃ (4.15-9.45%), and low contents of TiO₂, MnO, MgO, Na₂O, K₂O and P₂O₅. The XRD analysis of mud samples indicated mineral compositions with major minerals of quartz, illite, calcite, chlorite, feldspar, kaolinite, and other minor minerals like halite, smectite, fluorapatite, pyroxene, amphibole. The organic and physicochemical parameters of mud samples were also measured. Potentially toxic elements in mud samples were determined and compared with reference values and the technical standard. This study proposes that saline mud samples from the studied area are potential peloids.

Keywords: East Vietnam Sea, peloid, mud, total organic carbon, pH, cation exchange capacity.

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1. Introduction

The definition and application of peloid have been shown in many publications (Ahmad and Nicholas, 2009; Carretero and Pozo, 2009; Carretero et al., 2010; Quintela,

2012; Gomes et al., 2013; Khiari et al., 2014; Moraes et al., 2017; Glavas et al., 2017). In these works, the authors have pointed out the main effects of peloids in therapy and cosmetics through peloids' mineralogical, geochemical, and physicochemical features. The term "peloid" has been used so far. For

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instance, Gomes et al. (2013) proposed the definition of peloid as a slurry or slurry with medicinal or cosmetic properties, covering consisting of a mixture of fine-grained materials, mineral water, or seawater, and organic compounds from biological metabolism. Peloid has both natural and artificial origin, and concerning composition, includes inorganic, organic, and mixed types. According to practical applications, peloid has been used for medical purposes as well as cosmetics. Carretero et al. (2010) mentioned that peloid is a natural product consisting of a mixture of organic and inorganic materials with the sea, salt lake, or mineral-medicinal water after maturation and can be applied for therapeutic or cosmetic purposes. Saline mud played a vital role as an essential material used for peloids.

The East Vietnam Sea (EVS), one of the largest marginal seas in the western North Pacific, is a prospective case for studying saline mud (Shakirov et al., 2020). In recent years, many studies have been intensively carried out and focused on oil and gas potential, solid minerals like Fe-Mn crust and nodule, REEs in the northern, central, and southern parts of the sea (Petro Vietnam, 2005; Tan et al., 2009; To et al., 2009; Luong and Hoang, 2019). In addition, some studies reported data on clay mineralogy (Sang et al., 2020), and heavy minerals (Jagodziński et al., 2020; Long et al., 2021) in the western EVS.

In Vietnam, healing muds have been used mainly in some spas and resorts. However, studies on mud, in general, and peloid, in particular, have been few to date (Nghiep, 2014; Xuan et al., 2016; Man et al., 2020). Noticeably, there is no available data on saline mud in the EVS and its application as potential peloids. As mentioned above, many previous studies indicated the main effects of peloids in therapy and cosmetics through peloids' mineralogical, geochemical, and physicochemical characteristics. More recently, saline mud was highly recommended as the suitable material used for therapeutic purposes (Glavas et al., 2017) based on the investigation of those features. Consequently, this study aims to present the chemical, mineralogical, and physicochemical features of saline mud from the southwestern subbasin of the EVS (Fig. 1). Based on this data, the use of mud samples for cosmetic and therapeutic purposes from the studied area has been proposed.

2. Geological setting

The opening of the East Vietnam Sea, which is situated at the junction of the Eurasian, Pacific, and Indo-Australian plates (Li et al., 2015), occurred in Cenozoic with oceanic floor extension that started about 32 Ma and ended about 15.5 or 16 Ma (Oligocene-Miocene) as suggested in Li et al. (2015), Hoang (2020), and references therein.

As a part of the EVS, the southwestern sub-basin of the EVS (Fig. 1) is located in the southern part of the Vietnam continental shelf, wide in extension and low in gradient (Schimanski and Stattegger, 2005). This area includes the southwestern sub-basin of the EVS and the eastern part of the Nam Con Son basin. It has been attracted the attention of many scientists, mainly focused on geological and geophysical fields (Petro Vietnam, 2005; Phach et al., 2018). According to Li et al. (2015), the southwestern sub-basin has a spreading ridge extending 400 km southwestward between 23.6 and 16 Ma.

Sang et al. (2020) indicated that the Southeast Asia contributes considerable sediment to the EVS and the Mekong River is one of the most important sources. Particularly, the Mekong River's sediment discharge to the southern part of the EVS is 166 Mt/year (Sang et al., 2020). Schimanski and Stattegger (2005) estimated the sedimentation rates for the Holocene along the

Vietnam Shelf. They showed that the southern shelf has low values of 5-10 cm/ky (25-40 cm/ky in sheltered areas) of sedimentation rates. Sang et al. (2020) emphasized the important role of the Mekong River in contribution terrigenous sediments to

the studied area. Meanwhile, according to To et al. (2009), the surface sediments in the studied area are terrigenous sandy mud, abyssal siliceous ooze, and continuously hemipelagic and abyssal calcareous ooze from shallow to the deeper parts.

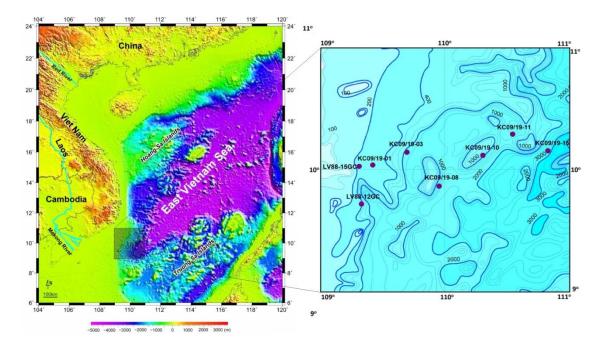


Figure 1. Studied area in the East Vietnam Sea and sampling locations

3. Material and method

Mud samples presented in this study were taken on board from 8 gravity cores during the expeditions in the EVS of two cruises of DK105 in August and September 2019 and Lavrentyev in November 2019. These cruises were within the framework of the Vietnam National project KC09/16-20 and joint-project "First joint expedition on marine geophysicsgeology-oceanography between VAST and FEBRAS by Akademik Lavretyev the East Vietnam Sea" QTRU.02.05/19-20, respectively. The location and water depth of gravity cores and the interval of each sample in the core are shown in Figure 1 and Table 1, respectively. All samples were then contained in plastic bags and preserved in a refrigerator

until the pre-treatment procedure for geochemical analysis.

Eight mud samples were dried up in the temperature room and then ground to powder using an agate mortar. All analysis of major elements, trace elements was carried out at Laboratory of Rock and Geochemistry, Department of Physics and Earth Sciences, University of the Ryukyus. Major elements (including SiO₂, TiO₂, Al2O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅) were determined using a ZSX Primus II XRF on glass beads. All powdered samples were placed in ceramic crucibles and baked for 10 hours insight a KDF heater at 900°C to eliminate all surface water and organic material. LOI (loss on ignition) measurement, the baked powders were

weighed and compared with the original powder before glass bead preparation. Each 1g heated sample powder was mixed with 5g flux of Li-tetraborate Li₂B₂O₇ (ratio 1:5) in a platinum crucible for making the glass bead. The mixture was heated at 800°C and 1200°C respectively in 2 minutes and 5 minutes using a TK-4200 Bead & Fuse-Sampler. The glass beads were then cooled down and transferred to XRF for major element determination. To verify the accuracy and precision of the analytical method, one USGS standard sample, BHVO-2 was also analyzed along with eight samples, and the analytical result of BHVO-2 showed good agreement with the certified result.

An X series-2 ICP-MS (Thermo Fisher Scientific) was utilized to analyze potentially toxic trace elements (Table 2). A set of 46 trace elements was determined from the analysis, and 15 potentially toxic trace elements including Ag, As, Ba, Bi, Cd, Cr, Cs, Co, Cu, Mo, Ni, Pb, Sb, Sr, and Zn, were in this study. For analytical selected preparation, about 50 mg of baked sample powder was weighed in a 15 ml Teflon beaker then dissolved by the mixture of HNO3 and HF (ratio 1:2). Next, all beakers were dried up on a hotplate at 120°C for two days. The dried samples were then dissolved in 1ml 15 M HNO₃ and evaporated to dryness. This step was repeated twice to make sure all the samples were dissolved. Then, 3 ml 2M HNO₃ was added and left on a hotplate overnight at 80°C. Finally, about 0.164g sample solution was weighed and mixed with about 10.5-12.1g 0.3M HNO₃ to form a dilution factor of about 3982-4040. For the ICP-MS analysis, blank and geological standard samples of BHVO-2, JB-1a, JA-2 were prepared to make a calibration curve and verify analytical accuracy.

An Empyrean-PANalytical XRD was utilized for mineralogy analysis at 45 Kv, 40 mA at the Institute of Geological Sciences, Vietnam Academy of Science and

Technology. The samples were first dried up at 60°C and then ground to the grain size of 0.01 mm. The HighScore Plus software was used to process the XRD phases for calculating the semi-quantitation of minerals.

Grain-size analysis of the samples was performed at the Institute of Geological Sciences, Vietnam Academy of Science and Technology, using a Horiba laser scattering particle size distribution analyzer LA-960, which can analyze the grain size 0.01 to 5000 µm. The samples were first dried up in a temperature room and then dispersed in distilled water in 30 minutes using a magnetic stirrer. All samples were ultrasonically treated before the grain-size measurement of the machine.

For bulk organic geochemistry of mud samples, the parameters of total organic carbon (TOC), protein, total sulfur (TS), total nitrogen (TN) were determined. The TOC was determined following the Walkley Black method (TCVN-8941:2011). The organic carbon compound in the mud sample was oxidized with a potassium dichromate solution in concentrated sulfuric acid. The excess potassium dichromate was titrated by Fe (II) salt solution. Besides, the Kjeldahl method was applied for protein analysis (TCVN-10791:2015). Accordingly, nitrogen compound in the mud sample was digested using hot, concentrated sulfuric acid to obtain ammonium sulfate. The decomposed product was then mixed with sodium hydroxide solution, and ammonia released by distillation into the boric acid solution. Finally, the ammonia was titrated with a standard acid solution. Besides, the TS and TN were also determined according to TCVN-9296:2012 and TCVN-6498:1999.

The physicochemical parameters of pH and density were determined by applying TCVN-5979:2007 and TCVN-6863:2001. Besides, the cation exchange capacity (CEC) index was determined by the ammonium acetate method (TCVN-8568:2010).

Additionally, the gravimetric method was applied to determine the mud sample's water content and dry residue (TCVN-6648:2000). All mud samples were dried up in a hot conditioner at 105°C±5°C. Before and after the sample drying procedure, the mass differences were calculated for the water content and dry residue.

4. Results

The analytical result of XRF, XRD, and ICP-MS analysis for mineralogy, major, and trace elements of the eight samples are presented in Tables 1, 2, 4 respectively.

Table 1 indicates that mud samples have the highest contents of SiO₂ among major elements, ranging from 32.79 to 48.09%, an average of 39.42%. The concentrations of Al₂O₃ and Fe₂O₃ are in ranges of 11.26-13.63% and 4.15-9.45%, respectively, and exhibit lower values compared with those of

the commercial peloid from Italy (Cara et al., 2000) but higher than those of saline mud samples A and B from Slovenia (Glavas et al., 2017). The CaO contents vary in a relatively wide range from 3.10% to 13.93%. Other major elements, for instance, TiO₂, MnO, MgO, Na₂O, K₂O, and P₂O₅, have low concentrations (Table 1).

The mineral compositions of mud samples (Table 2, Fig. 2) have the ranges of quartz (28-53%), calcite (5-31%), illite (16-31%), chlorite (5-13%), feldspar (5-13%), kaolinite (3-8%), halite (1-5%), smectite (<1%). The compositions of quartz and calcite show relatively good agreement with major element compositions like SiO_2 and CaO, respectively, resulting in a proportional correlation between them (Fig. 3). Besides, some other minerals are fluorapatite, pyroxene, amphibole with low contents and rare appearance.

Table 1. Major element compositions of saline mud samples

	Depth	Interval	SiO ₂	TiO ₂	Al ₂ O ₂	Fe ₂ O ₂	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Na ₂ O/
Sample	(m)	(m)	(wt%)	(wt%)			(wt%)	_		_	_	2 3	-
LV88-12GC-1	263	0.3-0.4	48.09	0.65	12.74	4.74	0.06	2.11	4.84	1.70	2.33	0.09	0.35
LV88-15GC	236	0.9-1	44.33	0.62	12.68	4.54	0.06	2.16	6.61	1.87	2.00	0.10	0.28
KC09/19-01-1	296	0.1-0.3	47.57	0.67	13.62	5.04	0.06	2.02	3.10	1.73	2.52	0.09	0.56
KC09/19-03-1	1113	0.2-0.4	34.83	2.17	11.32	9.45	0.13	6.41	6.94	2.55	2.01	0.68	0.37
KC09/19-08-1	1985	0.2-0.4	37.04	0.51	12.54	4.50	0.18	2.20	9.27	2.19	1.58	0.11	0.24
KC09/19-10-1	1373	0.2-0.4	32.79	0.45	11.26	4.15	0.12	1.99	13.93	1.92	0.92	0.10	0.14
KC09/19-11-1	2015	0.2-0.4	35.00	0.48	12.10	4.21	0.25	2.10	12.22	2.11	1.19	0.10	0.17
KC09/19-15-1	3112	0.2-0.4	35.71	0.49	12.31	4.28	0.12	2.05	12.26	1.93	1.20	0.10	0.16
* CP			55.39	0.85	19.78	7.28	0.17	3.01	0.89	1.95	1.19	0.1	2.19
** Sample A	•		39.74	0.43	7.53	3.40	0.04	2.97	10.72	4.95	1.66	0.06	0.47
** Sample B			37.62	0.49	9.01	3.97	0.05	3.62	13.88	3.46	2.01	0.07	0.25

^{*}CP: Commercial peloid (Cara et al., 2000)

Table 2. Mineral composition of saline mud samples

Depth Into		Intorvol	Mineral composition (%)										
Sample	(m) (m)	(m)	Quartz	Calcite	Halite	Illite	Chlorite	Feldspar	Kaolinite	Fluorapatit	Amphibole	Pyroxene	Smectite (Montmorillonite)
LV88-12GC-1	263	0.3-0.4	53	5	1	19	10	5	6	1			<1
LV88-15GC	236	0.9-1	34	8	1	31	10	7	8				<1
KC09/19-01-1	296	0.1 - 0.3	35	14	2	16	9	10	7	2	3	2	<1
KC09/19-03-1	1113	0.2-0.4	32	14	3	21	8	13	5			4	<1
KC09/19-08-1	1985	0.2-0.4	34	23	4	17	6	9	6				1
KC09/19-10-1	1373	0.2-0.4	28	31	4	16	7	7	6				1
KC09/19-11-1	2015	0.2-0.4	30	26	5	24	6	5	3				1
KC09/19-15-1	3112	0.2-0.4	32	29	5	19	5	5	5				<1

^{**}Data from Glavas et al. (2017)

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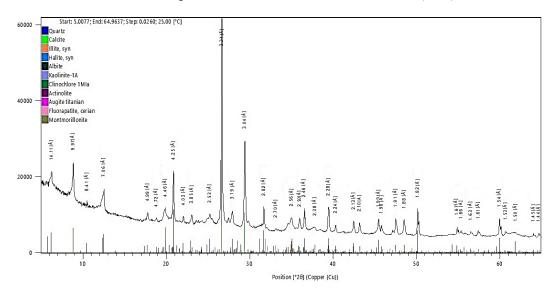


Figure 2. An example of XRD pattern of sample KC09/19-01-1

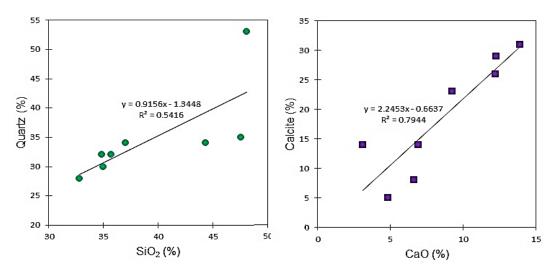


Figure 3. Correlation between Quartz and SiO₂, Calcite and CaO

The grain-size result of mud samples of clay (65.1-89.2%) and silt (9.5-89.2%) is presented in Fig. 4 and Table 3. 34.2%) particles over sand (0.35-1.63%) The most striking feature is the dominance particles.

Table 3. Grain-size parameters of saline mud samples

	I		F			
Sample	Depth (m)	Interval (m)	Mean	Md	So	Sk
LV88-12GC-1	263	0.3-0.4	8.78	2.47	2.49	2.17
LV88-15GC	236	0.9-1	8.40	2.48	2.32	1.62
KC09/19-01-1	296	0.1-0.3	7.59	2.40	1.86	2.23
KC09/19-03-1	1113	0.2-0.4	4.53	2.41	1.61	1.04
KC09/19-08-1	1985	0.2-0.4	4.67	2.38	1.48	1.02
KC09/19-10-1	1373	0.2-0.4	6.87	2.22	1.47	1.07
KC09/19-11-1	2015	0.2-0.4	4.47	2.02	1.38	1.00
KC09/19-15-1	3112	0.2-0.4	5.29	1.88	1.40	1.01

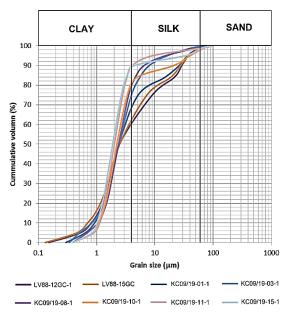


Figure 4. The grain-size cummulative curves of mud samples in the studied area, measured by a Horiba laser scattering particle size distribution analyzer LA-960

The trace element concentrations of mud samples are presented in Table 4 with 15 identified elements, including Ag, As, Ba, Bi, Cd, Cr, Cs, Co, Cu, Mo, Ni, Pb, Sb, Sr, and Zn. Among them, highly toxic elements like As, Cd, and Pb get the most attention. Their concentrations are in ranges of 6.38-20.23 ppm, 0.05-0.23 ppm, and 1.97-8.60 ppm for As, Cd, and Pb, respectively (Fig. 5). Generally, there is no

significant change of trace element concentrations from shallow the part (oxidizing environment) to the deeper part (reducing environment). On the other hand, Table 4 also shows the mean values of trace element concentrations of Cd, Cr, Cu, Ni, Pb, Zn in sediments of Can Gio mangrove forest (CGM), which is situated between an estuarine system of Dong Nai-Sai Gon river and a part of Vam Co river (Hung et al., 2019). The result reveals that sediments of CGM have the mean values of Cd. Cr. Cu. Ni. Zn concentrations in ranges of those in mud samples from this study, except the case of Pb concentrations with significantly higher value (26.6 ppm compared with 1.97-8.60 ppm).

From the analytical results of bulk organic geochemistry (Table 5), mud samples have TOC, protein, TS, and TN values in the range of 0.36-1.45%, 0.31-0.52%, 0.137-2.339%, and 0.072-106%, respectively. Table 5 shows the important results of physicochemical parameters, for instance, pH, density, CEC, water content, dry residue. The pH values vary in a narrow range, from 7.95 to 8.11. Besides, the density of mud samples ranges from 2172 to 2405 kg/m³. The important parameter of CEC exposes relatively high values, ranging from 73.74-87.36 cmol/kg. Notably, CEC, pH, and protein values reveal insignificant changes with depths (Fig. 6). The water content and dry residue have fairly wide ranges of 35.6-59.31% and 40.69-64.4%, respectively.

<i>Table 4</i> . Trace element compositions of saline mud sam	ples ((ppm))
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table 1. Trace clement compositions of same mad samples (ppm)															
Sample	Ag	As	Ba	Bi	Cd	Cr	Cs	Co	Cu	Mo	Ni	Pb	Sb	Sr	Zn
LV88-12GC-1	0.06	20.23	659	0.35	0.13	136.4	13.62	25.33	38.16	32.67	68.85	8.52	1.72	463.1	96.6
LV88-15GC	0.04	6.38	411.2	0.28	0.05	90.16	6.97	16.63	26.49	0.64	48.95	4.21	0.87	392.9	68.9
KC09/19-01-1	0.08	7.79	605.8	0.56	0.09	133.8	6.15	25.06	29.76	0.85	76.05	3.51	1.34	653.7	127.1
KC09/19-03-1	0.11	7.22	917.6	0.43	0.12	126.4	7.65	25	34.14	0.82	91.85	3.57	2.07	601.4	116.8
KC09/19-08-1	0.13	8.56	1531	0.67	0.12	135.6	1.56	32.05	39.27	0.81	133	8.60	2.88	833.2	154.8
KC09/19-10-1	0.09	6.85	1334	0.80	0.14	108.5	0.39	26.99	32.98	0.73	123.9	1.97	2.94	1010	201.2
KC09/19-11-1	0.11	8.84	1698	1.0	0.18	121.2	0.59	30.98	37.86	0.8	128.2	2.16	2.35	1011	217
KC09/19-15-1	0.12	9.06	1759	0.95	0.23	137.7	1.01	36.26	44.55	0.86	142.8	2.25	3.12	1024	216.8
* CGM's sediment					0.07	102.5			26.5		50.6	26.6			107.2
** Sample A	0.12	9.80	124	0.30	0.18	90		10.50	27.89	5.56	56.50	20.61	0.59	266	70.30
** Sample B	0.08	8.60	151	0.30	0.18	80		11.90	30.79	2.35	71.40	26.22	1.01	794	85.10
*** Spanish peloids range	<6	4.4-29.6	148-799	<1-3.3	<10	14.6-68.2	<6-28.5	4-16.8	11.5-52.3	<1-4.4	34-50.8	10.9-37.5	<2.37-4.3	87.3-1879	33.1-160.4
*** Turkish peloids range	< 0.1	5.1-62.6	110-1153	< 0.1-0.7	0.1-0.2	61.6-547.4	3.6-39.8	9.1-54.5	12.4-32.2	0.2-1.2	27-67.1	6.9-38.2	<0.1-1.2	214.3-1540.4	33-56
06/2011/TT-BYT		5										20			
Health, Canada		3			3							10	5		
European Medicine						<25			<250	<25	<25			·	<1300
Agency (2008)															

^{*}Mean values of trace element concentrations in sediments of the Can Gio mangrove forest (Hung et al., 2019);

^{**}Data from Glavas et al. (2017); *** Data from Carretero et al. (2014)

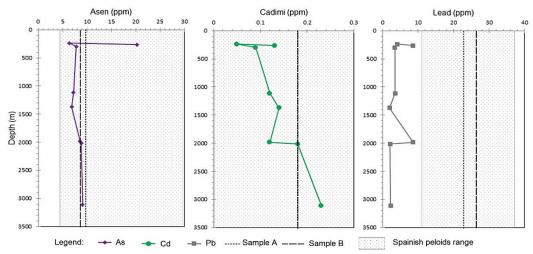


Figure 5. Vertical profiles of As, Cd, Pb of mud samples in comparison with reference values of saline mud samples from Slovenia (Sample A and sample B; Glavas et al., 2017), peloids from Spain (Carretero et al., 2014)

Table 5. Bulk organic geochemical and physicochemical parameters of saline mud samples

]	Parameter										
Sample	TOC (%)	Protein (%)	TS (%)	TN (%)	рН	Density (kg/m³)	Cation exchange capacity (cmol/kg)	Water content (%)	Dry residue (%)			
LV88-12GC-1	1.09	0.41	2.339	0.078	8.06	2405	76.00	35.60	64.40			
LV88-15GC	1.09	0.44	0.563	0.072	8.11	2345	80.75	46.85	53.15			
KC09/19-01-1	1.45	0.39	0.137	0.095	8.07	2300	74.24	47.09	52.91			
KC09/19-03-1	1.09	0.45	0.261	0.106	8.03	2205	73.74	58.96	41.04			
KC09/19-08-1	1.27	0.52	0.240	0.106	8.04	2172	81.25	59.31	40.69			
KC09/19-10-1	0.36	0.34	0.220	0.078	8.01	2172	86.21	58.33	41.67			
KC09/19-11-1	0.91	0.31	0.254	0.078	7.95	2192	80.03	58.80	41.20			
KC09/19-15-1	0.73	0.31	0.192	0.072	8.01	2190	87.36	55.87	44.13			
*Sample A	1.96	0.24	1.41	0.15	7.93	1516	249.9	44	56			
*Sample B	0.89	0.04	2.53	0.12	8.52	1478	161.5	50	50			
**Spanish peloids range						1114-1562	11-112	31.43-76.64	25.36-68.57			
***Commercial peloids							12.8; 14.0; 120.0					

^{*}Data from Glavas et al. (2017); **Data from Carretero et al. (2014); ***Data from Quintela et al. (2012)

5. Discussions

The major element compositions of mud samples in the studied area (Table 1) are similar to those of 2 saline mud samples collected from the northern Adriatic Sea, which was suggested as a suitable material for therapy applications (Glavas et al., 2017). The sample KC09/19-03-1 exposed significantly higher TiO₂, Fe₂O₃, P₂O₅ compared with those

of other samples. The Na₂O/CaO ratio of 8 samples is low (<1), thus much smaller than that of commercial peloids (Cara et al., 2000). However, this ratio is similar to that of coastal mineral mud, saline mud in Turkey and Slovenia (Karakaya et al., 2010; Kalkan et al., 2012; Glavas et al., 2017). In addition, it was also observed in bentonite samples from various worldwide places in Italy, Spain,

Argentina, and Vietnam (Cara et al., 2000; Carretero et al., 2010; Baschini et al., 2010; Man et al., 2020).

The analytical results (Table 2) showed that the mud samples' dominant minerals were quartz, calcite, and illite. Cara et al. (2000a, 2000b) reported mud minerals with a high clay mineral content, such as the smectite group, with high expansion capacity, specific surface area, and high cation exchange capacity. However, saline mud samples with high quartz, calcite, and illite still have high therapy applicability. According to Glavas et al. (2017), the presence of quartz and calcite contribute usefully applying physiotherapy and beauty technology. Small quartz and calcite particles stimulate or modulate mechanisms that promote better health (Mihelčić et al., 2012). Nissenbaum et al. (2002) pointed out that the famous Dead Sea black mud products have carbonate minerals greater than 60% and are used in physiotherapy and beauty treatments. More importantly, Quintela et al. (2012) reported some peloids in use at Italian and Spanish spas, with high quartz, calcite, and illite contents. Therefore, the above clay mud samples still have the potential for use in physiotherapy and beauty treatment.

For pelotherapy, cosmetic and pharmaceutical purposes, the product from mud and clay sediment must be satisfied for user safety. Especially toxic elements like Cd, Pb, and As must be under the allowable limit. Table 4 presents trace element compositions of mud samples and other reference values of saline mud samples from Slovenia (Glavas et al., 2017), peloids from Spain, and Turkey (Carretero et al., 2014), along with allowable limits of heavy metals of some technical standards. Generally, potentially elements of mud samples in these studies are relatively similar to those of two saline mud samples in Glavas et al. (2017) which were suggested as a suitable material therapeutic purposes. On the other hand, it is noted that toxic elements are not permitted in cosmetic products (Carretero et al., 2010; Glavas et al., 2017). This study utilized heavy metal guidance for the cosmetic products of Health, Canada (2012) and Circular No. 06/2011/TT-BYT of Ministry of Health (Table 4). Obviously, all Cd, Pb, and Sb contents are under the allowable limit while those of As exceed the permissible limit. Besides, Cu, Zn, and Mo meet requirement of limits for pharmaceutical formulations (European Medicine Agency, 2008) while Cr and Ni completely exceed. However, Carretero et al. (2010) studied the mobility of elements in the interaction between artificial sweat and peloids and pointed out that the elements leached in higher concentrations are Na, Ca, Mg, and K elements that were not leached or leached in deficient concentrations. Noticeably, authors reported that the content of the potentially toxic elements (Ag, As, Be, Cd, Hg, Pb, Sb, Se, Tl, and Zn) in the leached extracts is negligible. In addition, Table 4 and Fig. 5 show that toxic elements like As, Cd, and Pb completely have concentrations in the ranges of Spanish and Turkish peloids (Carretero, 2014).

The grain-size result of mud samples expresses the highest amount of clay particles in the range of 65.1-89.2%, while silt particles vary from 9.5% to 34.2%. The amount of sand particles is negligible, ranges 0.35-1.63%. The fine-grained mud is very appropriate when applied to the skin (Glavas et al., 2017). This result supports that the mud samples are very suitable for peloid-like therapeutic purposes.

The TOC contents of mud samples from the studied area vary from 0.36% to 1.45%, comparable to those reported in Glavas et al. (2017). Besides, protein contents (Table 5) exhibit a relatively high value, ranging from 0.31-0.52%, making the mud sample more suitable for therapeutic purposes. The amount of TS with low values from 0.192-0.563% appears with almost mud samples, except in sample LV88-12GC-1 (2.339%), which may relate to hydrothermal activity-derived sulfur-

rich compounds at the station LV88-12GC. This high TS value is relatively similar to those reported in Glavas et al. (2017), between 1.41% and 2.53%. However, together with the high concentrations of As, Mo, and LV88-12GC-1 sample recommended in use for peloids. The TN contents exhibit low values from 0.072% to 1.106%, and no anomalous value these observed. Consequently, organic geochemical parameters reinforced the suitability of mud samples in this study for peloids, except in the case of sample LV88-12GC-1.

Concerning physicochemical parameters, the pH values of mud samples vary from 7.95 to 8.11. According to Glavas et al. (2017), the pH range of 4 to 8 is advisable to avoid skin irritations; thus, mud samples in this study have pH values within this range. On the other hand, these pH values are closely similar to those recommended as suitable for peloids (e.g., Carretero et al., 2014; Glavas et al., 2017; Man et al., 2020). Figure 6 indicates that pH values of mud samples are totally in the range of saline mud samples A and B (Glavas et al., 2017). One of the most critical parameters is CEC, ranging from 73.74-87.36 cmol/kg in this study (Table 5). These

CEC values are relatively high compared with previous studies (Cara et al., 2000; Quintela et al., 2012; Carretero et al., 2014; Man et al., 2020). Glavas et al. (2017) showed that a higher CEC value allows for saline mud's higher capacity to trap potentially toxic elements from water, essential for therapeutic benefits. Besides, according to Man et al. (2020), high CEC values allow an exchange of nutrients in contact of peloid with skin and clear skin through the absorption of toxins, bacteria, and unwanted substances of the peloid from the skin. Figure 6 shows that CEC values of mud samples in this study are relatively high compared to reference values of commercial peloids (Quintela et al., 2012), peloids from Spain (Carretero et al., 2014), thus confirming the potential use of mud samples for peloids.

Noticeably, these mud samples have significantly higher protein contents than those of saline mud samples A and B from Slovenia (Fig. 6). This high amount of protein will take good effect when applied to the skin. In addition, the values of density (2172-2405 kg/m³), water content (35.60-59.31%), and dry residue (40.69-64.40%) of mud samples make them suitable for peloids in comparison with reference values (Table 5).

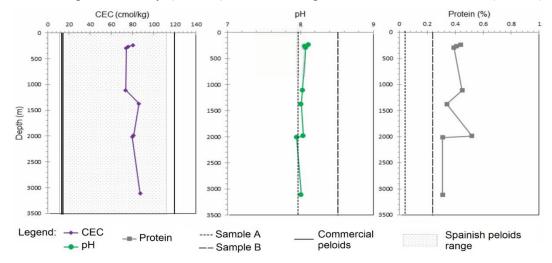


Figure 6. Vertical profiles of CEC, pH, protein of mud samples in comparison with reference values of saline mud samples from Slovenia (Sample A and sample B; Glavas et al., 2017), commercial peloids (Quintela et al., 2012), peloids from Spain (Carretero et al., 2014)

6. Conclusions

Eight saline mud samples from the southwestern sub-basin of the East Vietnam Sea were analyzed for chemical. mineralogical, physicochemical compositions to assess the suitability of peloids. The analytical result of major elements shows the highest contents of SiO₂ (32.79-48.09%), CaO (3.10-13.93%), and Al_2O_3 (11.26-13.63%). The XRD analysis exposes the dominance of quartz, illite, calcite over other minor minerals. Trace elements (Ag, As, Ba, Bi, Cd, Cr, Cs, Co, Cu, Mo, Ni, Pb, Sb, Sr, Zn) in mud samples were determined and compared with those of reference values and technical standard. Potentially toxic elements of mud samples in these studies are relatively similar to those of two saline mud samples in Slovenia and completely in the ranges of Spanish and Turkish peloids. The grain-size analysis reveals that fine-grained mud samples are very suitable for peloids. The organic parameters, including TOC, TS, and TN, are reasonably suitable for peloids. Sample LV88-12GC-1 with a high amount of TS and high concentrations of As, Mo, Pb, which relate to hydrothermal activity-derived sulfur-rich compounds, is not recommended in use for peloids. The mud samples have relatively high CEC in the range of 73.74 -87.36 cmol/kg, acceptable pH value (7.95-8.11), and a high amount of protein (0.31-0.52%). Consequently, saline mud samples from the studied area as potential peloids were proposed, except in sample LV88-12GC-1.

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References

Ahmad A.F., Nicholas E.P.Jr., 2009. Low levels of toxic elements in Dead Sea black mud and mud-derived cosmetic products. Environ Geochem Health, 31, 487-492.

Anders E., Grevesse N., 1989. Abundances of the elements: Meteoritic and solar. Geochimica et Cosmochimica Acta, 53, 197-214.

Cara S., Carcangiu G., Padalino G., Palomba M.. Tamamini M., 2000. The betonites in pelotherapy: chemical. mineralogical and technological properties of materials from Sardinia deposits (Italy). Applied Clay Science, 16, 117-124.

Carretero I.M., Pozo M., 2009. Clay and non-clay minerals in the pharmaceutical industry. Part I. Excipients and medical applications. Applied Clay Science, 46, 73-80.

Carretero I.M., Pozo M., Martin-Rubi J.A., Pozo E., Maraver F., 2010. Mobility of elements in interaction between artificial sweat and peloids used in Spanish spas. Applied Clay Science, 48, 506-515.
Carretero M.I., Pozo M., Legido J.L., Fernandez-Gonzalez M.V., Delgado R., Gomez I., Armijo F., Maraver F., 2014. Assessment off three Spanish clays for their use in pelotherapy. Applied Clay Science, 99, 131-143.

Circular No. 06/2011/TT-BYT. Regulation on management of cosmetics. Ministry of Health. Ha Noi, 2011.

European Medicine Agency, 2008. Guideline on the specification limits for residues of metal catalysts or metal reagents. Available at: https://www.ema.europa.eu/en/documents/scientific-

- guideline/guideline-specification-limits-residuesmetal-catalysts-metal-reagents en.pdf.
- Glavas N., Mourrelle M.L., Gomez C.P., Legido J.L., Smuc N.R., Dolenec M., Kovac N., 2017. The mineralogical, geochemical, and thermophysical characterization of healing saline mud for use in pelotherapy. Applied Clay Science, 135, 119-128.
- Gomes C., Carretero M.I., Pozo M., Maraver F., Cantista P., Armijo F., Legido J.L., Teixera F., Rautureau M., Delgado R., 2013. Peloids and pelotherapy: Historical evolution. classification and glossary. Applied Clay Science, 75-76, 28-38.
- Health, Canada, 2012. Guidance on heavy metal impurities in cosmetics. Available at: https://www.canada.ca/en/health-canada/services/consumer-product-safety/reports-publications/industry-professionals/guidance-heavy-metal-impurities-cosmetics.html.
- Hoang N., 2020. Geodynamic context and mantle source of the East Vietnam Sea spreading-related volcanic rocks in Vietnam and neighboring areas. Journal of Geology, Series A, 317-372/2020, 21-38.
- Hung T.T, Huyen D.T., Tu T.A, Desmet M., 2019.
 Presence of trace elements in sediments of Can Gio mangrove forest, Ho Chi Minh city, Vietnam.
 Vietnam Journal of Earth Sciences, 41(1), 21-35.
- Jagodziński R., Sternala B., Stattegger K., Szczuciński W., 2020. Sediment distribution and provenance on the continental shelf off the Mekong River, SE Vietnam: Insights from heavy mineral analysis. Journal of Asian Earth Sciences, 196, 1-16.
- Kalkan E., Canbolat M.Y., Yarbasi N., Ozgul M., 2012. Evaluation of thermal mud characteristics of Erzurum (Koprukoy) clayey raw materials (NE Turkey). International Journal of Physical Sciences, 7(40), 5566-5576.
- Karakaya M.C., Karakaya N., Sarioglan S., Koral M., 2010. Some properties of thermal muds of some spas in Turkey. Applied Clay Science, 48, 531-537.
- Khiari I., Mefteh S., Sanchez-Espejo R., Cerezo P., Aguzzi C., Lopez-Galindo A., Jamoussi F., Iborra C.V., 2014. Study of traditional Tunisian medina clays used in therapeutic and cosmetic mud-packs. Applied Clay Science, 101, 141-148.
- Li C.-F., Lin J., Kulhanek D.K., the Expedition

- Scientists, 2015. Proceedings of the International Ocean Discovery Program Volume 349. Expedition 349 summary, 43pp.
- Long H.V., Thanh N.T., Tuan V.T., Tung N.T., Anh N.L, Din D.B, Duc L.V., Dien T.N., Hiep N.H., 2021. Holocene sedimentation offshore Southeast Vietnam based on geophysical interpretation and sediment composition analysis. Vietnam Journal of Earth Sciences, 43(3), 336-379.
- Luong L.D, Hoang N., 2019. Distribution of rare earth elements and methane concentrations in the East China Sea water column: A comparison with the East Vietnam Sea (Bien Dong). Conference proceedings on Advanced Researches in the Earth and Environmental Sciences (Carees 2019). Publishing House of Natural Sciences and Technology, 128-131.
- Man T.T., Lan T.T., Duong N.A., Anh P.L., 2020.
 Assessment of the usability of Tam Bo bentonite (Di Linh, Lam Dong) for peloid. Vietnam Journal of Earth Sciences, 42(4), 384-394.
- Mihelčić G., Kniewald G., Ivanišević G., Čepelak R., Mihelčić V., Vdović N., 2012. Physico-chemical characteristics of the peloid mud from Morinje Bay (eastern Adriatic coast, Croatia): suitability for use in balneotherapy. Environ. Geochem. Health, 34, 191-198.
- Moraes J.D.D., Bertolino S.R.A., Cuffini S.L., Ducart D.F., Bretzke P.E., Leonardi G.R., 2017. Clay minerals: Properties and applications to dermocometic products and perspective of natural raw materials for therapeutic purposes A review. International Journal of Pharmaceutics, 534, 213-219.
- Nghiep V.C., 2014. Mineral water, industrial water, mineral mud. Encyclopedia of Geology. Editors: Tong Duy Thanh, Mai Trong Nhuan, Tran Nghi, 451-458.
- Nissenbaum A., Rullkötter J., Yechieli Y., 2002. Are the curative properties of black mud from the Dead Sea due to the presence of bitumen (asphalt) or other types of organic matter? Environ. Geochem. Health, 24, 327-335.
- PetroVietnam, 2005. Geology and oil and gas resources of Vietnam, 526pp.

- Quintela A., Terroso D., Silva E.F.D., Rocha F., 2012.Certification and quality criteria of peloids used for therapeutic purposes. Clay minerals, 47, 441-451.
- Sang P.N., Bat D.V., Hiep N.H., Chi N.T.K., Binh P.V., 2020. Characteristics of sediment provenance in the southwestern East Sea. Journal of Mining and Earth Sciences, 61(5), 11-19.
- Schimanski A., Stattegger K., 2005. Deglacial and Holocene evolution of the Vietnam shelf: stratigraphy, sediments and sea-level change. Marine Geology, 214, 365-387.
- Shakirov R.B., Cuong D.H., Obzhirov A.I., Thanh N.T., Valitov M.G., Lee N.S., Legkodimov A.A., Kalgin V.Y., Eskova A.I., Proshkina Z.N., Telegin Y.A., Anh L.D., Storozhenko A.V., Ivanov M.V., Luong L.D., Pletnev S.P., Syedin V.T., Shvalov D.A., Lipinskaya N.A., Bovsun M.A., Makseev D.S., Nhon D.H., 2020. The first integrated Russian-Vietnamese geological, geophysical and oceanographic expedition in the East Vietnam Sea (88th cruise of the R/V Akademik M.A. Lavrentiev, October 27 - December 08, 2019). Results of expeditionary research in 2019 in the World Ocean, inland waters and on the Svalbard archipelago. Conference proceedings, February 26-27, 2020 Moscow. Russian Federation. ISBN 978-5-6044865https://doi.org/10.21072/978-5-0-4. 144-162. 6044865-0-4 (in Russian).
- Tan M.T. (Ed), et al., 2009. The East Vietnam Sea. Marine Geology and Geophysics. The Publishing

- House of Science and Technology. Vietnam Academy of Science and Technology, 3, 517pp.
- Taylor S.R., McLennan S.M., 1995. The geochemical evolution of the continental crust. Review of Geophysics, 33(2) 241-265.
- TCVN-10791:2015. Malt-Determination of the nitrogen content and calculation of the crude protein content Kieldahl method.
- TCVN-5979:2007. Soil quality-Determination of pH.
- TCVN-6498:1999. Soil quality-Determination of total nitrogen-Modified Kjeldahl method.
- TCVN-6648:2000. Soil quality-Determination of dry matter and water content on a mass basic Gravimetri method.
- TCVN-6863:2001. Soil quality-Determination of particle density.
- TCVN-8568:2010. Soil quality-Method for determination of cation exchange capacity (CEC) by ammonium acetate method.
- TCVN-8941:2011. Soil quality Determination of total organic carbon Walkley Black method.
- TCVN-9296:2012. Fertilizers-Method for determination of total sulfur-Gravimetric method.
- To L.D (Ed), et al., 2009. The East Vietnam Sea.
 Overview on the East Vietnam Sea. The Publishing
 House of Science and Technology. Vietnam
 Academy of Science and Technology, 1, 316pp.
- Xuan P.T., Lien N.T., Dang P.T., Pho N.V., Tra D.T., Nga H.T., Quynh B.V., 2016. The nature of the phenomenon of "mud eruption" in Ninh Thuan. Vietnam Journal of Earth Sciences, 38(1), 90-97.