



## Formulation of muds for pelotherapy: effects of “maturation” by different mineral waters

Fernando Veniale<sup>a</sup>, Elisabetta Barberis<sup>b</sup>, Gianfranco Carcangiu<sup>c</sup>, Noris Morandi<sup>d</sup>,  
Massimo Setti<sup>a,\*</sup>, Massimo Tamanini<sup>c</sup>, Daniel Tessier<sup>e</sup>

<sup>a</sup>*Dipartimento Scienze della Terra, University of Pavia, via Ferrata 1, Pavia I-27100, Italy*

<sup>b</sup>*Dipartimento DI.VA.PRA-Chimica Agraria, University of Turin, Turin, Italy*

<sup>c</sup>*Centro Studi Geominerari e Mineralurgici CNR (Consiglio Nazionale delle Ricerche), Cagliari, Italy*

<sup>d</sup>*Dipartimento Scienze della Terra e Geologico-Ambientali, University of Bologna, Bologna, Italy*

<sup>e</sup>*Laboratoire Science du Sol-INRA, Versailles, France*

Received 26 June 2003; received in revised form 29 September 2003; accepted 7 October 2003

Available online 30 December 2003

### Abstract

Spa centres in northern Italy use clayey admixtures for the formulation of muds to be used in pelotherapy. The basic ingredient (“virgin” clay) is a dressed bentonitic geomaterial with mineralogical composition: smectite 60–70%, illite 5–10%, kaolinite 10–15%, quartz 5–10%, calcite 5–10% and feldspars 2–3%.

The peloid muds are obtained by “maturation” of the virgin clay with mineral waters gushing out in situ which have different geochemistry: sulphureous, Ca-sulphate, Ca–Mg-sulphate and Br–I-salty (after the Italian regulation DPR 105/92). The maturation treatment is varying with respect to the mixing procedure and lasting time.

Peculiar parameters have been tested to verify the effects of various maturation treatments, i.e., changes with respect to virgin clay.

Formation of organic matter is due to the presence of microorganisms and algae in the maturation habitat. The <2 μm fraction is generally decreased due to clay particles agglomeration. Mineralogical changes are mainly concerning the degradation of clay minerals, as smectite and illite, and subordinately to the dissolution of calcite. Cation exchange capacity (CEC), soluble salts, water retention, swelling index, activity, consistency parameters (WL, WP and PI), thermal behaviour and cooling kinetics are influenced by the geochemistry of mineral waters used for the maturation treatments but with some opposite trends for Br–I-salty water, and for sulphureous and Ca-sulphate waters, respectively.

Noteworthy was the influence of high-pH value of the virgin clay on the pH of peloid muds (in fact, the pH of the used mineral waters is ranging around the natural value). Furthermore, the temperature reached by the peloid muds after 20 min of application (calculated after an innovative mathematical model) is influenced by water retention. An increase in plasticity index and a slower cooling are considered to improve the quality of the obtained peloid muds for pelotherapy.

The observed different cation exchange behaviour and soluble salt content could be discriminant for either dermatological masks or thermal body cataplasms.

\* Corresponding author. Fax: +39-382-505890.

E-mail address: [setti@crystal.unipv.it](mailto:setti@crystal.unipv.it) (M. Setti).

A need of regulation (standard procedures) is suggested to certificate the clay geomaterials suitable for pelotherapy and also for drugs formulation.

© 2003 Elsevier B.V. All rights reserved.

*Keywords:* Peloid muds; Maturation treatments; Mineral water effects; Application selectivity; Certification protocol

---

## 1. Introduction

There is a long tradition in using clays as empirical medicine, and was also noticed by legends, beliefs, rituals and ethnological records. Geofagy (eating of earth or soil or clay) still persists not only as superstition or magic aspect (Reinbacher, 1999; Veniale, 1996).

Clay minerals as kaolinite, smectite and fibrous sepiolite–palygorskite are used in the preparation of pharmaceutical products and animal feed as active chemosorbents for protective coatings of stomach, intestine and skin (cosmetics, dermatology, burns treatment, etc.) and as adsorbents of toxins, bacteria and even viruses (Carretero, 2001; Veniale, 1992, 1997).

“Pelotherapy” is the local or generalized application of thermal muds (hot cataplasms called “peloids”) for recovering rheumatism, arthritis and bone–muscle traumatic damages. The recent development of cutaneous chemotherapy (treatments of seborrhoeic skin, antimicrobial and antifungal agents) has requested clay minerals with peculiar properties, aiming to realize new functional and durable medications (Martin-Diaz, 1998).

Thermal mud is a hyperthermal or hyperthermalized mud produced by the primary or secondary mixing of a solid component (usually a clayey geomaterial) with a mineral–thermal water. After suitable preparation (“maturation”), the mixing leads to the production of the therapeutic mud (“peloid”) that is used as a poultice in medical practice.

Nowadays, clay/water ratio, degree of maturation and workability of a peloid mud are matters of empirism, hitherto left to the judgement of the practitioner and not repeatable for different spas.

The maturation procedures applied in Italian spas have been described by various authors (see references in Calamita and Busi, 1972; Curini et al., 1990) and is known to occur through extremely complex

processes involving not only virgin clay/mineral water interactions but also biological and biochemical processes related to the growth of microorganisms and algae, depending on the habitat existing in the open-air tanks where the maturation is carried out.

To be suitable for thermal therapy, certain qualities of peloid muds are much appreciated: low-cooling rate, high-exchange capacity, good adhesivity, ease of handling and pleasant sensation when applied to the skin.

The main factors contributing to the peloid mud features are: composition and granulometry of the virgin clay, geochemistry of the mineral water, procedure of mixing and remixing each other, and the lasting time, the so-called “maturation” (Morandi, 1999; Veniale et al., 1999; Yvon and Ferrand, 1996).

As a matter of fact, the primary reserves of peloid muds are being exhausted around thermal springs; so, hydropathic and thermal centres have difficulty in obtaining supplies. Thus, they use argillaceous “virgin” geomaterials of foreign provenance mixed with salty mineral water(s) gushing in situ.

The aim of our investigation was: (i) to evaluate the effect of different mineral waters and maturation procedures on the minerals constituting the virgin geomaterial; (ii) to determine the physicochemical properties and rheological behaviour of matured muds; (iii) to put in evidence the need of regulations (standard criteria) for certifying the characteristics of clay geomaterials usable for the formulation of peloid muds suitable for differentiated pelotherapies and dermatologic applications.

## 2. Materials

In order to gain insights of the peculiar properties of peloid muds prepared in several spa centres of northern Italy by maturation of the same virgin clay geomaterial mixed with different mineral waters gush-

ing in situ, the following analyses have been carried out: granulometry, mineralogy, chemistry, physico-chemistry (pH, exchange capacity, soluble salts), consistency, activity, water retention, swelling index, thermal behaviour and cooling kinetics.

The obtained data concerning the matured muds have been compared with those of the “virgin” clay geomaterial and mineral waters.

The *investigated materials* are:

	V	Virgin clay	Spa centres
Mud sample	M1a	treated with sulphureous water	Salice Terme/PV
	M1	treated with Br–I-salty water	Salice Terme/PV
	M2		Negrini spa-Salice/PV
	M3		Rivanazzano Terme/PV
	M4	treated with Ca-sulphate water	Angolo Terme/BS
	M6		San Pellegrino Terme/BG
	M5	treated with Ca–Mg-sulphate water	Boario Terme/BS

The *basic ingredient (virgin clay)* used for the preparation (by maturation) of the peloid muds is the same for the various spa centres.

It consists of a dressed bentonitic geomaterials (supplied by the firm SO.MI.ES., Genoa-Italy) having the mineralogical composition:

Smectite 60–70%	Clay minerals
Illite 5–10%	
Kaolinite 10–15%	
Quartz 5–10%	Associated phase
Feldspar 2–3%	
Calcite 5–10%	

The smectitic constituent is Na<sup>+</sup> exchanged (basal reflection at 12.4 Å).

X-ray diffraction traces of the bulk geomaterials and its <2 µm fraction are given in Fig. 1; its chemical composition is reported in Table 1.

Different *mineral waters* are used for the maturation of the investigated peloid muds; they are classified (after the Italian Regulation DPR 105/92) as: sulphureous, Ca-sulphate, Ca–Mg-sulphate and Br–I-

salty. Their main physicochemical characteristics are reported in Table 2.

### 3. “Maturation” procedures

The procedure of mixing the admixture of virgin clay with mineral water, and the lasting time (“maturation” treatment) for obtaining the peloid mud is somewhat different in the investigated spa centres.

Usually, the virgin clay is being mixed in open air with the mineral water using basins with roughly cubic shape and volume of about 8–10 m<sup>3</sup>. The mineral water should be in excess with respect to the clay moisture degree; in fact, a layer of water (few centimeters thick) should permanently cover the clay/water admixture. The paste is periodically being remixed during the maturation lasting time; this operation is different in the various spa centres.

*Salice Terme/PV*: muds M1a (sulphureous water) and M1 (Br–I-salty water). Maturation treatment is lasting 1 year with remixing of the paste every 2 weeks. After maturation, the mud is heated at 120 °C (sterilisation) in silos. For the body application, the mud temperature is lowered at 48 °C.

*Negrini spa-Salice/PV*: mud M2 (Br–I-salty water). Maturation time: 6 months. Heating, sterilising and application temperatures are similar to Salice Terme (see above).

*Rivanazzano Terme/PV*: mud M3 (Br–I-salty water). Maturation time: 2 years without remixing. Before body application, heating at 42–45 °C in small pails (volume: 15 l).

*Angolo Terme/BS*: mud M4 (Ca-sulphate water). Maturation time: 2 years with daily remixing by mechanic shovels. Heated at 60 °C in oven and then transferred by pails (15 l) to the application room where the therapy is performed at 42–45 °C.

*San Pellegrino Terme/BG*: mud M6 (Ca-sulphate water). Maturation time: 1 year with continuous remixing by worm-screw. Heating by “bain-marie” device at about 50 °C and body application at 48 °C.

*Boario Terme/BS*: mud M5 (Ca–Mg-sulphate water). Maturation time: 6 months with the addition of humus and vegetable organic matter coupled with continuous remixing by paddle wheel. Heating

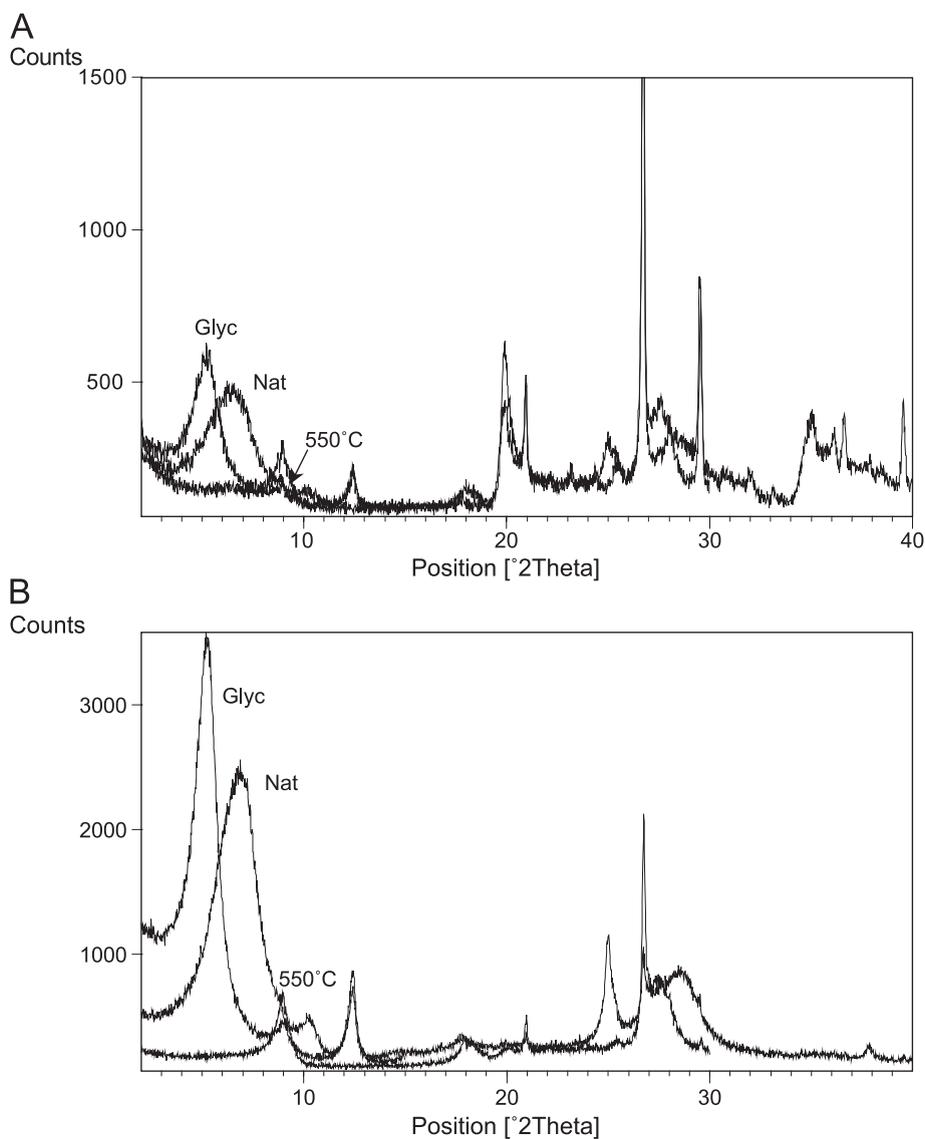


Fig. 1. XRD traces of bulk virgin clay (A) and its <2 μm fraction (B).

in silos at 60–70 °C and body application at 45–50 °C.

#### 4. Analytical methodologies and procedures

The *chemical compositions* has been determined by X-ray fluorescence analysis (XRF) after the methodology and procedure suggested by Franzini et al. (1975), and using a spectrometer Philips PW-1480.

The analyses have been courteously performed by Prof. L. Leoni at the Department of Earth Sciences, University of Pisa (Italy).

The *mineralogical composition* of the bulk sample (random powder) and fraction <2 μm (oriented specimen) has been estimated by X-ray diffractometry (XRD) after routine procedures (Moore and Reynolds, 1997; Wilson, 1987): (i) at room temperature and relative humidity; (ii) after solvation in atmosphere of ethylene–glycol at 60 °C/5 h; and (iii) after heating

Table 1  
Chemical composition of virgin clay

Essential elements	Percentage (%)	Trace elements (ppm)			
SiO <sub>2</sub>	49.76	As 3	La 31	Ni 49	
Al <sub>2</sub> O <sub>3</sub>	17.56	Pb 24	Ce 66	Cr 115	
Fe <sub>2</sub> O <sub>3</sub>	6.54	Hg n.d.	Ga 25	V 160	
FeO	n.d.	Cd n.d.	Nb 15	Co 24	
MnO	0.12	Se n.d.	Zr 123	Cu 44	
MgO	2.38	S 368	Y 18	Zn 91	
CaO	2.76	Cl 200		Ag n.d.	
Na <sub>2</sub> O	1.26	Ba 177		Sb n.d.	
K <sub>2</sub> O	1.35	Sr 397		Sn n.d.	
TiO <sub>2</sub>	0.77	Rb 81			
P <sub>2</sub> O <sub>5</sub>	0.09				
LOI	17.00				

n.d. = not determined.

at 550 °C/2 h. XRD traces were performed with a Philips PW-1800 diffractometer (Cu-radiation). Identification of the crystalline phases were carried out by a search–match system and their quantification applying the Syroquant software (Taylor and Clapp, 1991).

The *grain-size analyses* (granulometry) have been carried out after the Norm ASTM-D422: previous humid sieving for the separation of the sand fraction from the silt-clay ones and further densitometry of the water dispersion (added with Calgon to avoid flocculation) for detailing the distribution of the finer fractions.

*Physicochemical parameters* as pH, cation exchange capacity (CEC) and soluble salts have been estimated after the procedures of Italian Ministry of Agriculture (1994): “Metodi ufficiali di analisi chimica del suolo”.

*Consistency parameters* [liquid limit (WL), plastic limit (WP) and plastic index (PI)] have been determined after the Norm CNR-UNI n. 10014.

*Thermal analyses* [Differential Thermal Analysis (DTA), Thermo-Gravimetric Analysis (TGA) and Derivative of TGA (DTGA); i.e., weight-loss rate] have been performed with a Setaram TAG-24 instrument, both in air and CO<sub>2</sub> atmosphere (to avoid effects due to carbonate breakdown).

*Swelling index*, i.e., the volume (ml) reached by 2 g of smectitic clay after dispersion in distilled water,

Table 2  
Main physicochemical characteristics of mineral waters

Mineral water classification	Sulphureous	Br–I-salty			Sulphate		
		Ca	Ca–Mg				
Peloid mud samples	M1a	M1	M2	M3	M4	M6	M5
Source temperature (°C)	12.2	17.4	14	14	18	19.8	15.1
pH	7.1	6.9	6.6	7.3	7.5	7.1	7.0
Electric conductivity (at 20 °C; in $\mu\text{S cm}^{-1}$ )	3050	89,900	77,600	32,300	2321	2360	2260
Solid residue (at 180 °C; in mg/l)	2905	73,312	62,688	24,456	2579	2642	2465
CO <sub>2</sub> (cm <sup>3</sup> /l)	21	16	120	99	12	11	25
HCO <sub>3</sub> (bicarbonate)	428	210	164	633	210	22,507	283
Sulphidric degree (mgH <sub>2</sub> S/l)	33	95	n.d.	n.d.	<0.02	<0.02	<0.01
Nitrogen (mg/l)	0.28	50	66	50	<0.05	<0.10	<0.05
Sulphate	1119	82	10	28	1600	1556	1462
Chloride	653	44,308	38,900	16,900	2.5	36	7
Bromide	2	243	200	105	<0.5	<0.20	<0.05
Iodide	<0.5	23	9	30	<0.5	0.10	<0.5
Fluoride	0.63	0.97	0.1	0.4	0.56	0.23	n.d.
Borate	6	147	n.d.	578	<1	<0.1	<0.05
Na <sup>+</sup>	556	23,740	17,300	7950	12	23	8
K <sup>+</sup>	11	207	146	52	2	2	2
Ca <sup>2+</sup>	294	2292	2360	239	408	62	553
Mg <sup>2+</sup>	128	1371	n.d.	n.d.	192	n.d.	74
Li <sup>+</sup>	0.13	4	2	1	0.037	0.07	0.03
Sr <sup>2+</sup>	6	370	222	35	10	8	12
Ba <sup>2+</sup>	6	6	18	6	<0.02	0.02	<0.05

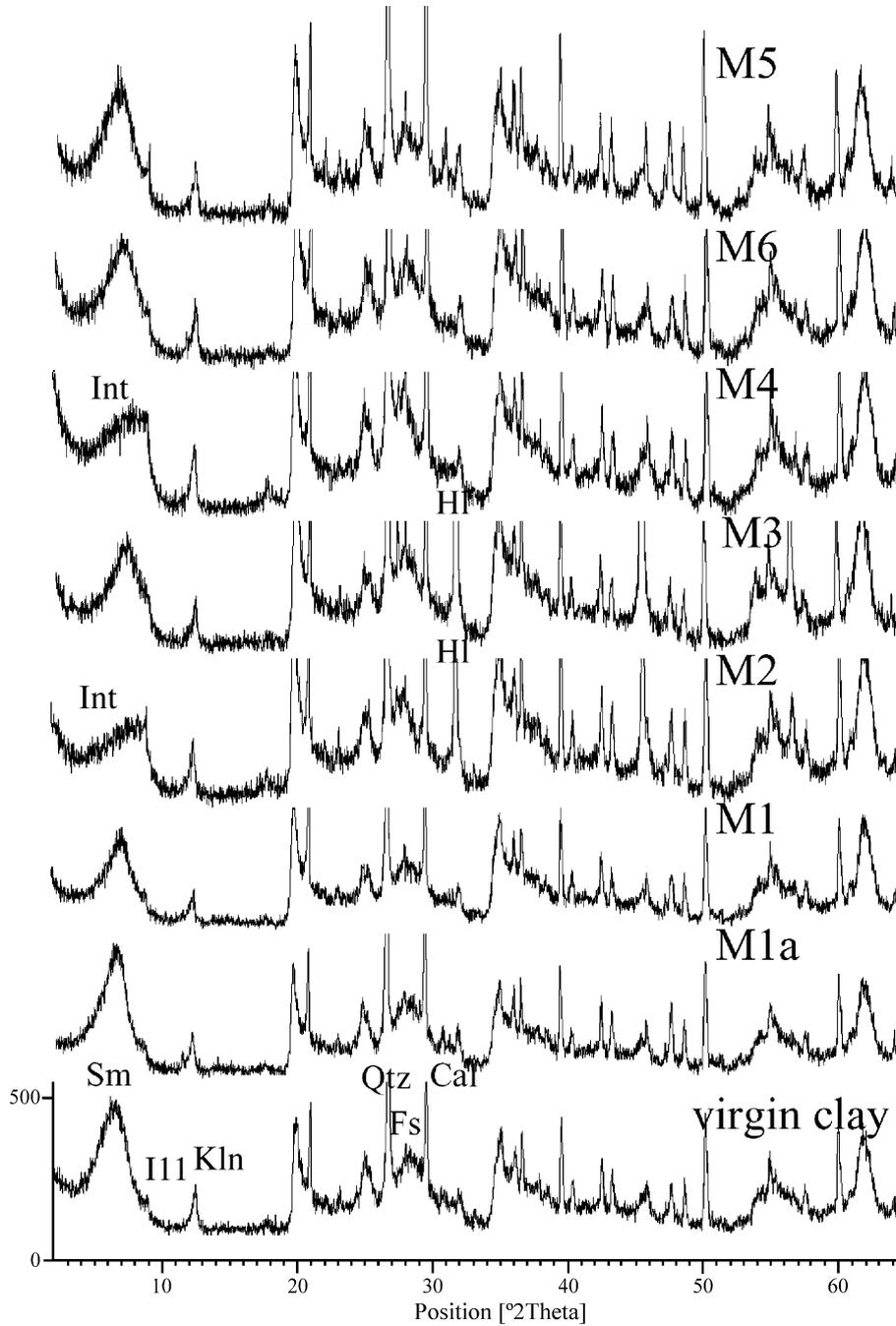


Fig. 2. XRD traces of virgin clay and peloid muds. Sm: smectite; Int: intergrades; Ill: illite; Kln: kaolinite; Qtz: quartz; Fs: felspar; Cal: calcite; HI: halite (mineral symbols after Kretz, 1983).

Table 3  
Mineralogical composition (semiquantitative) of virgin clay and peloid muds

	Clay minerals				Associated phases			
	Sm	Int	Ill	Kln	Cal	Qtz	K-fs	Pl
V	60	0	10	10	10	7	1	2
M1a	70	0	5	10	5	7	1	2
M1	65–70	5	5	5–10	5–10	7	0	0
M2	60	5–10	5–10	10	5	7	1	2
M3	65–70	5	5	5–10	5	7	1	2
M4	60	5–10	5–10	10	5	7	1	2
M6	65–70	5	5	10	<5	7	0	0
M5	65–70	5	5	10	5–10	7	1	2

Sm: smectite; Int: intergrades; Ill: illite; Kln: kaolinite; Cal: calcite; Qtz: quartz; K-fs: K-felspar; Pl: plagioclase (mineral symbols after Kretz, 1983).

was measured after the procedure described by Novelli and Marani (1976).

*Water retention* (i.e., water contents at different matric potential) were measured using a pressure membrane apparatus (Tessier et al., 1992). Water content is expressed with respect to the dry mass of the sample after oven-drying at 105 °C for 24 h.

*Cooling kinetics* was examined using a novel simple apparatus that allows to measure the moisture conditions during the application of a cataplasm to the body skin (Cara et al., 1999). A mathematical model based on theoretical equations describing the thermal exchange between a hot body in contact with a cool

body with infinite heat capacity, when applied to the experimental measures, allows the apparent heat capacity (i.e., cooling kinetics) of the peloid mud to be obtained by a best fit regression.

## 5. Experimental results

The *mineralogical changes* induced by the various maturation treatments (Fig. 2: XRD traces; Table 3: mineralogical composition) are mainly concerning clay minerals and, subordinately, calcite.

With respect to virgin clay, the smectite amount is slightly increasing in the peloids muds, whereas illite is decreasing, as for calcite. Exceptions are muds M2 and M4 exhibiting a “plateau” between 14 and 10 Å that indicates the presence of “intergrades” (Rich, 1968); this could be due both to the different mineral waters and different maturation procedures.

The basal reflection around 12 Å is somewhat broadened with respect to virgin clay (and the peloid mud M1a, matured with sulphureous water). As referring to calcite (generally decreasing), only the muds matured with Ca- and Ca–Mg-sulphate waters contain a higher amount.

Maturation treatments caused the formation of organic matter as indicated by the exothermic peak within the range 300–400 °C of the DTA curve (see example in Fig. 3) due to the presence of organic

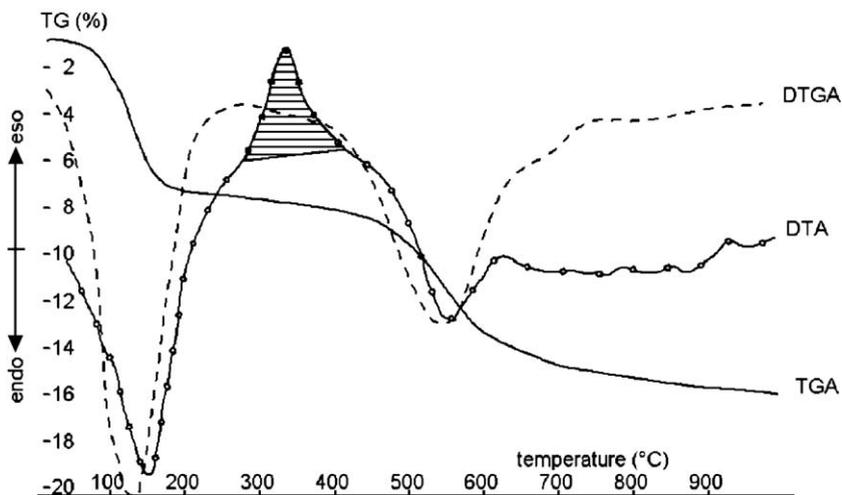


Fig. 3. Thermal analyses curves performed in CO<sub>2</sub> atmosphere of peloid mud M1 matured with Br–I-salty water. Noteworthy was the presence of an exothermic peak in the DTA curve due to the presence of organic matter.

matter that is absent in the virgin clay. A similar weak exothermic shoulder is also present in the DTA curves of peloid muds M3, M4 and M5.

The *granulometry* (Table 4) of virgin clay was modified by the various maturation treatments; in fact, the amount of  $<2 \mu\text{m}$  fraction in peloid muds is generally decreasing (indicating some agglomeration of the fine clay particles), especially in peloid muds matured with Br–I-salty and Ca–Mg-sulphate waters.

The *consistency parameters* (Table 4) are strongly influenced by the different maturation treatments but with opposite trends. Peloid muds matured with Br–I-salty waters (samples M1, M2 and M3) and with sulphureous water (sample M1a) show lower values in comparison to virgin clay paste (distilled water); such trend is less evident for the peloid mud matured with Ca–Mg-sulphate water (sample M5). On the contrary, peloid muds matured with Ca-sulphate waters (samples M4 and M6) show higher values of WL, WP and PI.

Some *physicochemical parameter* results were modified by the different maturation treatments (Table 4).

Noteworthy was the high-pH value of virgin clay that influences those of peloid muds; in fact, the pH of mineral waters is ranging around the neutral value. Peloid muds matured with Br–I-salty waters that have relatively lower pH.

*Total cation exchange capacity* (CEC) of the peloid muds were significantly lowered by all the maturation treatments (Table 4), and such condition is probably to be referred to agglomeration of clay particles (as indicated by the grain-size analysis: decrease of fraction  $<2 \mu\text{m}$ ) that blocks some surface (re)active sites.

Surprisingly, the amount of discrete *exchangeable cations* of the peloid muds were higher with respect to virgin clay (in contrast with the decrease of total CEC); the only exception is the peloid mud matured with Ca–Mg-sulphate water (sample M5). The increase of exchangeable cations is especially pronounced for peloid muds matured with Br–I-salty

Table 4  
Physicochemical parameters of virgin clay and peloid muds

Samples	V	M1a	M1	M2	M3	M4	M6	M5
<i>Granulometry</i>								
Fraction $<2 \mu\text{m}$	85	80	75	78	73	82	81	75
<i>pH</i>								
Virgin clay and mud	9.9	9.4	9.1	8.3	8.6	9.7	9.4	9.6
Mineral water		7.1	6.9	6.6	7.3	7.5	7.1	7.0
<i>Cation exchange capacity (meq/100 g)</i>								
	63	55	49	52	61	51	55	50
<i>Exchangeable cations (meq/100 g)</i>								
Ca <sup>2+</sup>	16	17	21	23	14	15	16	18
Mg <sup>2+</sup>	4	7	8	10	9	6	7	6
K <sup>+</sup>	2	2	2	2	2	3	2	2
Na <sup>+</sup>	35	52	65	87	189	48	41	20
Total	57	78	96	122	214	72	66	46
<i>Soluble salts (<math>\mu\text{g/g}</math>)</i>								
Ca <sup>2+</sup>	9	16	395	712	350	2,125	10	11
Mg <sup>2+</sup>	15	4	90	350	250	0.5	2	4
K <sup>+</sup>	72	35	185	265	167	110	44	85
Na <sup>+</sup>	1250	900	4150	12,000	26,000	450	650	300
<i>Consistency parameters</i>								
Liquid limit (WL; %)	180	106	98	71	73	271	254	153
Plastic limit (WP; %)	27	13	28	28	22	25	29	36
Plastic index (PI)	153	93	70	43	51	246	225	117

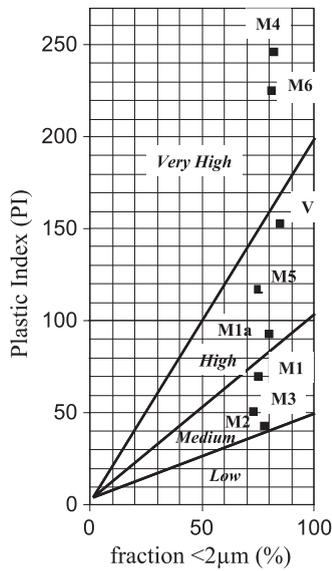


Fig. 4. Activity chart.

waters (samples M1, M2 and M3). Such behaviour could be ascribed not only to the different geochemistry of the mineral waters (see Table 2) but also to the different analytical procedures (disaggregation of the clay microaggregate by shaking) that makes free several active sites on the clay particle surface.

Soluble salts are relatively scarce in the virgin clay (Table 4) with the exception of Na<sup>+</sup> (due to the activation treatment during its dressing). Peloid muds

maturated with sulphureous (sample M1a) and Ca- and Ca–Mg-sulphate waters (samples M4, M6 and M5, respectively) show a decrease of soluble salts, with the exception of sample M4 (Ca-sulphate water) showing a very high value of Ca<sup>2+</sup>. Peloid muds maturated with Br–I-salty waters (sample M1, M2 and M3) show an evident increase of soluble salts especially of Na<sup>+</sup>. Such different behaviour is to be connected with the geochemistry of the mineral waters (Table 2).

The activity chart (Fig. 4), e.g., fraction <2 µm versus plasticity index, evidences the enhanced activity of peloid muds maturated with Ca-sulphate waters (samples M4 and M6) with respect to the virgin clay (that itself possesses a high activity). On the other hand, the activity has been lowered by other maturation treatments: it is still high for peloid muds maturated with sulphureous (sample M1a) and Ca–Mg-sulphate (sample M5) waters, whereas it drops to medium values for peloid muds maturated with Br–I-salty waters (samples M1, M2 and M3).

As concerning the water retention (Fig. 5), the peloid muds prepared by maturation with Br–I-salty waters (samples M1, M2 and M3) were “drier” than the virgin clay/distilled water paste; the same is true for peloid muds maturated with sulphureous (sample M1a) and Ca–Mg-sulphate (sample M5) waters although in a lesser degree. On the contrary, the peloid muds maturated with Ca-sulphate waters (samples M4 and M6) show the highest water retention (Fig. 5).

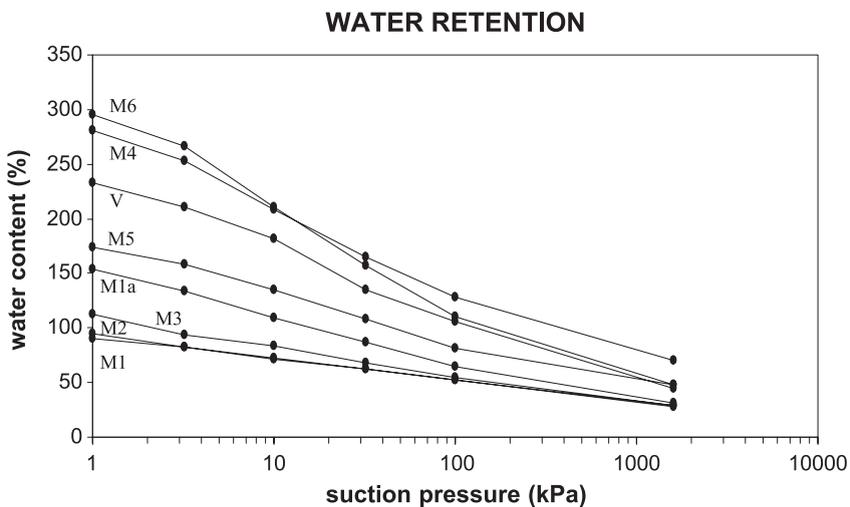


Fig. 5. Water retention curves of the peloid muds.

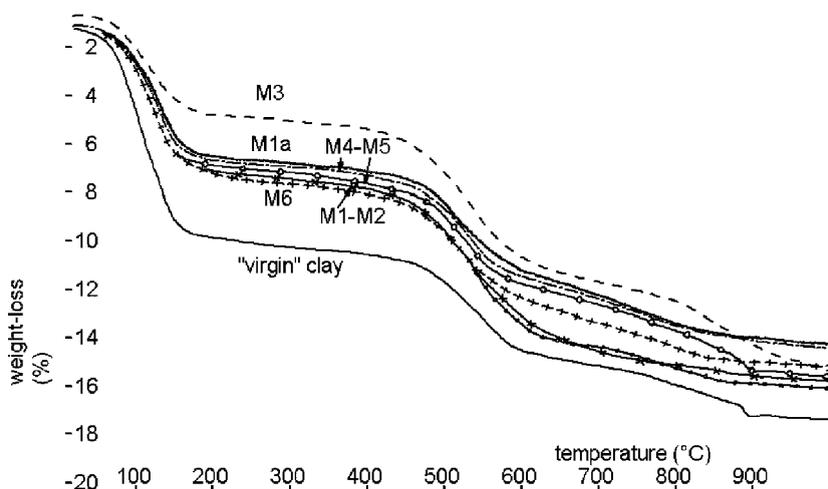


Fig. 6. Thermo-gravimetric (TGA) curves of the peloid muds performed in CO<sub>2</sub> atmosphere (see also Table 5).

The *thermal behaviour* has been investigated by thermal analyses and cooling kinetics.

The TGA curves (Fig. 6) shows an evidence of the reduction of water-loss within the temperature range 20–120 °C (hygroscopic water) for all the peloid muds with respect to the virgin clay/distilled water paste (see quantitative details in Table 5). Note the lowest value for the peloid mud M3 matured with a Br–I-salty water that possesses physicochemical characteristics different from other peloid muds (M1 and M2) prepared with similar waters (Table 2), namely, the lower values of chloride, bromide, sulphate, fluoride, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Sr<sup>2+</sup>, whereas pH, CO<sub>2</sub>, bicarbonate, borate and iodide are present in higher amounts. Moreover, the maturation procedure for the preparation of the peloid mud M3 is somewhat peculiar because the virgin clay/mineral water admixture is lasting 2 years without remixing.

Noteworthy was that Curini et al. (1990) have shown that the lasting time of maturation should at

least reach 6 months for producing changes in the thermal behaviour of the maturing paste.

The *cooling kinetics curves* (Fig. 7), together with the swelling index, moisture content and heat capacity (Table 6), show different behaviours for peloid muds matured with different mineral waters. Noteworthy was that only the peloid muds matured with Ca-sulphate waters (samples M4 and M6) possess a heat capacity higher than the virgin clay/distilled water paste, whereas this parameter is slightly lower for peloid muds matured with sulphureous (sample M1a) and Ca–Mg-sulphate (sample M5) waters. The peloid muds matured with Br–I-salty waters (samples M1, M2 and M3) show a more evident decrease of the heat capacity.

It is interesting to note how the temperature reached by the peloid muds after 20 min of application is influenced by the water retention (Table 6).

## 6. Discussion, interpretation and remarks

Investigation on the preparation procedures of muds for pelotherapy have only occasional references in the scientific literature, especially for the aspects concerning the solid argillaceous phase constituting the mud paste, its interaction with the mineral water used for the maturation treatment, and the related effects on mineralogical, physicochemical, rheological and thermal properties of the peloid muds. In fact,

Table 5

Loss of hygroscopic water (range 20–120 °C) calculated by TGA curves (Fig. 6)

Temperature range (°C)	V	M1a	M1	M2	M3	M4	M6	M5
20–1000	16.1	13.4	15.1	15.4	14.5	13.6	15.1	14.7
120–1000	11.1	10.8	12.1	12.5	12.5	10.7	12.1	11.4
20–120	5.0	2.6	3.0	2.9	2.0	2.9	3.0	3.3

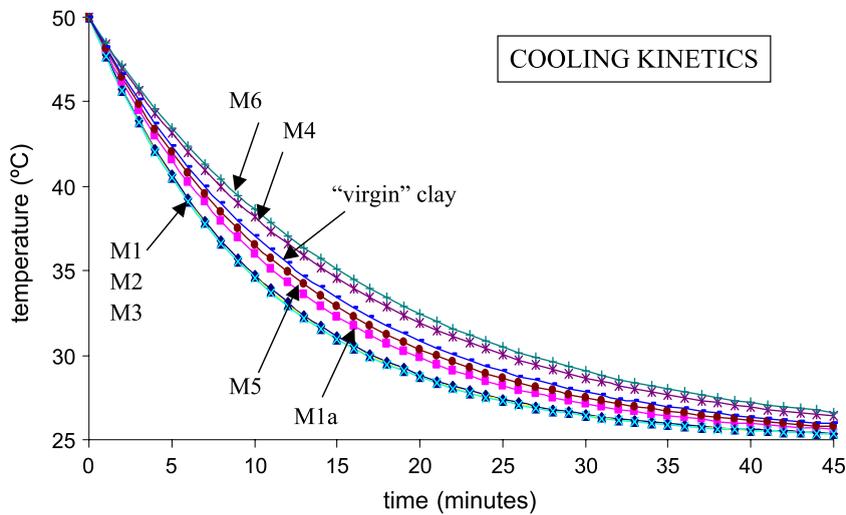


Fig. 7. Cooling kinetics curves of the peloid muds (see also Table 6).

the variability of these interacting factors is only rarely taken into account when considering the use for peliotherapeutic purposes.

Several references concerning investigations on peloid muds used in Italian spas have been selected: Bertelli (2000); Bertolani and Loschi-Ghittoni (1996); Calamita and Busi (1972); Cara et al. (2000); Curini et al. (1990); Jobstraibizer (1999); Magrini (1974); Marchesi and Padul (1963); Minguzzi et al. (1999); Summa and Tateo (1997).

Recently, Sanchez et al. (2002) have investigated the effect of maturation treatment (by a ferruginous, bicarbonate-rich and sulphate-rich water, and lasting

for different periods of time) upon the mineralogical and physicochemical properties of illitic–smectitic clays used for peliotherapy. The obtained results have shown a progressive degradation of clay minerals, with a reduction in the illite and smectite crystallinity, and in the smectite percentage and phyllosilicate content; furthermore, the percentage of  $<2 \mu\text{m}$  particles also decreased. These modifications caused changes in the physicochemical properties which are evidenced by an increase in the plasticity index and slower cooling of the peloid mud, both of which are considered as improving the clays' effect in peliotherapy.

For instance, Nissenbaum et al. (2002) have shown that the beneficial curative properties of the black clayey sediments of the Dead Sea are to be ascribed to their content of reduced sulphur species (brine) but not to the presence of organic matter (asphalt, bitumen). The black colour of the mud is rather due to the poorly crystallized iron sulphides.

The results obtained by our investigations (see also Veniale et al., 1999) evidence that the maturation treatments performed with different mineral waters and procedures have peculiar effects on the characteristics of peloid muds.

The sources of the mineral waters used by the investigated Italian spas are located in different geological environments: (i) the sulphureous and Br–I-salty waters are correlated to the evaporitic formation occurring along the northern Apennines strip; (ii) the

Table 6  
Swelling, moisture and heat capacity changes induced by different maturation treatments

	Swelling index (ml/2 g)	H <sub>2</sub> O (%)	C <sub>p</sub>	T <sub>20</sub>
V	15	61.0	2.69	31.98
M1a	9	53.2	2.38	31.19
M1	9	45.7	2.09	30.42
M2	8	44.8	2.05	30.33
M3	12	44.6	2.04	30.31
M4	15	70.3	3.05	32.93
M6	14	74.7	3.23	33.38
M5	10	57.2	2.54	31.60

C<sub>p</sub>: heat capacity; T<sub>20</sub>: temperature reached by the peloid mud after 20 min of application (calculated taking into account the moisture content).

Ca- and Ca–Mg-sulphate waters belong to sources located in the pre-Alps area.

Cation exchange capacity is modified (Table 3) especially by Br–I-salty and sulphureous water. Noteworthy was the high content of soluble salts after treatment with Br–I-salty waters (halite was also recognized as discrete phase; Fig. 2). The high content of  $\text{Ca}^{2+}$  in these mineral waters (Table 2) may favour the agglomeration of fine clay particles (Kjellander et al., 1988). In fact, the  $<2\ \mu\text{m}$  granulometric fraction is lowered especially by treatment with Br–I-salty waters (Table 4).

Mineralogical changes are mainly concerning clay minerals as smectite (transformed into “intergrades” by blockage of interlayer sites; Rich, 1968) and illite that is degraded (Fig. 2). Subordinately, calcite decreases with the exception of peloids muds matured with Ca- and Ca–Mg-sulphate waters where a higher content has been detected.

Some maturation treatments are coupled with the formation of organic matter (Fig. 3) originated either by metabolic product of microorganisms or by degradation of humus.

Consistency (Table 4) and activity (Fig. 4) are enhanced by treatment with Ca- and Ca–Mg-sulphate waters; other mineral water treatments are lowering these parameters.

Water retention (Fig. 5 and Table 6) denotes a better pathway for peloid muds matured with Ca-sulphate waters although showing high-moisture content. Remarkable is the low release of hygroscopic water (within the range 20–120 °C) (Table 5 and Fig. 6) by the peloid mud M3 (*Negrini spa*) to be ascribed to its peculiar maturation treatment: 2 years lasting time without remixing.

The cooling kinetics (Fig. 7) show different behaviours depending on the maturation waters; heat capacity is higher for peloid muds matured with Ca-sulphate waters and decreases significantly for maturation treatments with Br–I-salty waters. Noteworthy, the temperature reached by the peloid mud after 20 min of application is influenced by the water retention (Table 6).

Several parameters improving the peloid mud properties and behaviour during peliotherapeutic applications have to be underlined.

The surficial interactions between skin and peloid mud are influenced by the rheological and adhesive

properties which are driving the chemical and heat transfer.

The high-swelling index and water limit (Laird, 1999), plasticity, specific surface (due to the high percentage of  $<2\ \mu\text{m}$  clay fraction) and exchange capacity of bentonitic geomaterials make them suitable to improve the quality of peloid muds.

Thermal properties (Ferrand and Yvon, 1991) are considered as fundamental for peliotherapy because a good heat retention is required during the cataplasm application; in other words, a low-cooling rate is suitable for best benefit.

It is well known that pastes consisting of smectitic clay (“bentonite”)/mineral water admixtures are the best materials for thermal peliotherapy applications due to the ability of smectite to retain large water amounts (Morandi, 1999; Novelli, 2000; Yvon and Ferrand, 1996). In fact, a high-moisture content is an important factor for high-heat capacity.

Heat retention (dissipation) of peloid muds is depending on granulometry (specific surface) and water amount (moisture); the latter, in turn, is depending on smectite content because of its water retention capacity (Sala and Tessier, 1994). Noteworthy, smectites possess high and variable exchangeable cations which can largely range in hydration degree (Laird, 1999), thus influencing moisture and water diffusion (Güven and Pollastro, 1994).

The diffusion of water molecules in smectite pastes is influenced by the interstitial pore system and by their interaction with the surficial negative-charged sites of clay particles. The “diffuse double layer” occurring on the surface of clay particles, which is constituted of “dense” water molecules and more or less free cations, shows variable thickness (“osmotic” swelling) depending on kind and concentration of such cations. This layer of “bound” and less mobile “icelike” water (Sato, 1996; Tardy et al., 1999) covering the external surface of clay particles can represent an obstacle in the mobility of unbound water molecules within the pore spaces, and therefore reduce the water self-diffusion (Nakashima, 2003).

A mathematical model of cooling kinetics has been developed (Cara et al., 1999) that allows to predict the thermal behaviour of peloid muds. In such a way, the heat capacity and the temperature reached by the peloid mud after 20 min of application on the body skin can be easily calculated by the input into the

formulas of the measured moisture values. Moreover, these data are important in the spa management, especially when high-energy costs have to be met for the peloid mud heating.

The various and heterogeneous variables playing a role in the maturation process of peloid muds point out the need of protocols to “certificate” their quality taking into account the peculiar and different applications in thermal pelotherapy (thermal body cataplasms, dermatological masks, etc.). Currently, there is a lack of normative regulations about quality standards of the peloid muds.

A protocol has been developed for testing the bioadhesivity of peloid muds; it is based on innovative rheological and tensiometric approaches (Bettero et al., 1999). These parameters are important for evaluating the effectiveness of peloid mud applications on the body skin.

Other factors to be surveyed are:

- biological activity (living microorganisms and their metabolic products) developed during the maturation treatment (Ciferri, 1959; De Bernardi and Pedrinazzi, 1996; Galzigna et al., 1996);
- hazardous chemical elements (as As, Cd, Hg, Pb, Se, Tl, etc.) for their toxicity when scavenged by maturing waters and liberated from the peloid mud by the body-sweat leaching that is exerted during the pelotherapy application;
- radioactivity because of its production of dangerous ionising radiations (also volatile) that could remain into the lung tissues for a long time; a risk that is enhanced when the peloid mud is recycled, a common praxis in many spa centres.

The increasing success of natural health remedies is somewhat jeopardising (Veniale, 1996); not all that does glitter is gold!

## References

- Bertelli, M., 2000. Formulazione di matrici fangose ad uso termale e loro maturazione di condizioni controllate. Jobstraibizer P.G. and Bettero A. tutors, Thesis, Univ. Padua (Italy).
- Bertolani, M., Loschi-Ghittoni, A., 1996. I fanghi argillosi usati nelle terapie delle Terme della Salvarola (Sassuolo, MO). In: Veniale, F. (Ed.), Proc. Meeting “Argille curative” Salice Terme/PV, Gruppo Ital. AIPEA. Ed. Univ. Pavia, pp. 129–137.
- Bettero, A., Marazzan, M., Semenzato, A., 1999. Aspetti reologici e tensiometrici di matrici fangose di impiego termale e cosmetico. Proposta di un protocollo per la loro qualificazione. In: Veniale, F. (Ed.), Proc. Symp. “Argille per fanghi peloidi termale e per trattamenti dermatologici e cosmetici”. Montecatini Terme/PT, Gruppo Ital. AIPEA. Mineral. Petrogr. Acta, vol. XLII, pp. 277–286.
- Calamita, V., Busi, G., 1972. Sulla maturazione dei fanghi terapeutici e sui relativi impianti di produzione. Clinica Termale 27, 15–25.
- Cara, S., Carcangiu, G., Tamanini, M., 1999. Proprietà termiche dei fanghi termali bentonitici: proposta di una metodologia speditiva per un controllo di qualità. In: Veniale, F. (Ed.), Proc. Symp. “Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici”. Montecatini Terme/PT, Gruppo Ital. AIPEA. Mineral. Petrogr. Acta, vol. XLII, pp. 299–305.
- Cara, S., Carcangiu, G., Padalino, G., Palomba, M., Tamanini M., 2000. The bentonites in pelo-therapy: chemical, mineralogical, technological and thermal properties of clay pastes from Sardinia (Italy). Appl. Clay Sci., 16, 117–124, and 125–132 (see also Proc. 11th Int. Clay Conf. AIPEA, Ottawa 1997, 185–190).
- Carretero, M.I., 2001. Clay minerals and their beneficial effects upon human health. A review. Appl. Clay Sci. 21, 155–163.
- Ciferri, R., 1959. I fanghi terapeutici e la loro maturazione biologica. Atti Congr. Ass. Medica Ital. Idroclimatologia, Talassologia e Terapia Fisica, Perugia-Chianciano, vol. 2. Ed. AMIITTF, Rome, p. 11.
- Curini, R., D’Ascenzo, G., Fraioli, A., Laganà, A., Marino, A., Messina, B., 1990. Instrumental multiparametric study of the maturing of therapeutic muds of some Italian spas. Thermochem. Acta 157, 377–393.
- De Bernardi, M., Pedrinazzi, G.M., 1996. Azioni biologiche dei fanghi termali. In: Veniale, F. (Ed.), Proc. Meeting “Argille curative” Salice Terme/PV, Gruppo Ital. AIPEA. Ed. Univ. Pavia, pp. 17–24.
- Ferrand, T., Yvon, J., 1991. Thermal properties of clay pastes for pelotherapy. Appl. Clay Sci. 6, 21–38.
- Franzini, M., Leoni, L., Saitta, M., 1975. Revisione di una metodologia analitica per fluorescenza X basata sulla correzione completa degli effetti di matrice. Rend. Soc. Ital. Mineral. Petrol. 31, 365–368.
- Galzigna, L., Moretto, C., Lalli, A., 1996. Physical and biochemical changes of thermal muds after maturation. Biomed. Pharmacother. 50, 306–308.
- Guven, N., Pollastro, R.M., 1994. Clay-Water Interface and Its Rheological Applications Clay Miner. Soc., USA.
- Jobstraibizer, P.G., 1999. Definizione mineralogica e chimica del fango termale Eugenio. In: Veniale, F. (Ed.), Proc. Symp. “Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici”. Montecatini Terme/PT, Gruppo Ital. AIPEA. Mineral. Petrogr. Acta, vol. XLII, pp. 317–327.
- Kjellander, R., Marcelja, S., Quirk, J.P., 1988. Attractive double-layer interactions between calcium clay particles. J. Colloid Interface Sci. 126, 194–203.
- Kretz, R., 1983. Symbols for rock-forming minerals. Am. Mineral. 68, 273–279.
- Laird, D.A., 1999. Layer charge influence on the hydration of expandable 2:1 phyllosilicates. Clays Clay Miner. 47, 630–636.

- Magrini, D., 1974. Il Fango di Montecatini. Ed. Lito-Terme, Montecatini. 40 pp.
- Marchesi, E., Padul, F., 1963. Sul frazionamento dei granuli delle argille e il comportamento termico di alcuni fanghi terapeutici durante l'arco del processo maturativo. Ed. Terme e Clima, Brescia, Suppl., vol. I/3–4, pp. 3–13.
- Martin-Diaz, L., 1998. Arcillas, peloides y parafangos en medicina estetica. Master thesis, Univ. Islas Baleares (Spain).
- Minguzzi, N., Morandi, N., Tagnin, S., Tateo, F., 1999. Le argille curative in uso negli stabilimenti termali Emiliano-Romagnoli: verifica della composizione e delle proprietà. In: Veniale, F. (Ed.), Proc. Symp. "Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici". Montecatini Terme/PT. Gruppo Ital. AIPEA. Mineral. Petrogr. Acta, vol. XLII, pp. 287–298.
- Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd ed. Oxford Univ. Press, Oxford.
- Morandi, N., 1999. Thermal and diffractometric behaviour: decisive parameters for assessing the quality of clays used for healing purposes. In: Veniale, F. (Ed.), Proc. Symp. "Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici." Montecatini Terme/PT, Gruppo Ital. AIPEA. Mineral. Petrogr. Acta, vol. XLII, pp. 307–316.
- Nakashima, Y., 2003. Diffusion of H<sub>2</sub>O molecules in smectite gels: obstruction effect of bound H<sub>2</sub>O layers. *Clays Clay Miner.* 51, 9–22.
- Nissenbaum, A., Rullkötter, J., Yechieli, Y., 2002. Are the curative properties of "black mud" from the Dead Sea due to the presence or bitumen (asphalt) or other types of organic matter? *Environ. Geochem. Health* 24, 327–335.
- Novelli, G., 2000. La bentonite: un'argilla nei secoli al servizio dell'uomo. In: Fiore, S. (Ed.), *Incontri Scientifici*. vol. II Ed. Ist. Ricerche Argille-CNR, Potenza, pp. 207–304.
- Novelli, G., Marani, A., 1976. Regole internazionali temporanee sui metodi di controllo delle bentoniti impiegate come argille agglomeranti per fonderia. Ed. La Fonderia Italiana, Rome, vol. 2, pp. 47–48.
- Reinbacher, W.R., 1999. A brief history of clay in medicine. *Clay Miner. Soc. USA News*, 22–31.
- Rich, C.I., 1968. Hydroxy interlayers in expandable layer silicates. *Clays Clay Miner.* 16, 15–30.
- Sala, G.H., Tessier, D., 1994. Water retention by clayey materials: significance and prediction. *C.R. Acad. Sci. Paris* 318/II, 381–388.
- Sanchez, C.J., Parras, J., Carratero, M.I., 2002. The effect of maturation upon the mineralogical and physicochemical properties of illitic–smectitic clays for pelotherapy. *Clay Miner.* 37, 457–464.
- Sato, T., 1996. Hydration and structure of adsorbed water on clay minerals. *J. Miner. Soc. Japan* 25, 99–110.
- Summa, V., Tateo, F., 1997. The use of pelitic raw materials in thermal centres: mineralogy, geochemistry, grain-size and leaching tests. Examples from Lucania area (southern Italy). *Appl. Clay. Sci.* 12, 403–417.
- Tardy, Y., Mercury, L., Roquin, C., Vieillard, P., 1999. Le concepte d'eau "ice-like". *C.R. Acad. Sci. Serie 2, Sci. Terre et Planetes* 329, 377–388.
- Taylor, J.C., Clapp, R.A., 1991. New-features and advanced applications of Syroquant: a personal computer XRD full profile quantitative analysis software package. *Adv. X-ray Anal.* 35.
- Tessier, D., Lajudie, A., Petit, J.C., 1992. Relation between macroscopic behaviour of clays and their microstructural properties. *Appl. Geochem. (Suppl. 1)*, 151–161.
- Veniale, F., 1992. Clay science: facts and perspectives. Opening lecture of the "Veniale's day", Mediterranean clay meeting, Lipari-Aeolian isles. *Mineral. Petrogr. Acta* XXXV-A, 13–43.
- Veniale, F., 1996. Argille curative: antefatti, fatti e misfatti (Healing clays: previous facts, facts and wrong facts). In: Veniale, F. (Ed.), Proc. Meeting "Argille curative", Salice Terme/PV. Gruppo Ital. AIPEA, pp. 1–11.
- Veniale, F., 1997. Applicazioni e utilizzazioni medico-sanitarie di materiali argillosi (naturali e modificati). Corso di formazione "Argille e minerali delle argille–Guida alla definizione di caratteristiche e proprietà per usi industriali", Rimini, Gruppo Ital. AIPEA. Ed. IRTEC, Faenza, pp. 205–239.
- Veniale, F., Setti, M., Soggetti, F., Lofrano, M., Trailo, F., 1999. Esperimenti di maturazione di geomateriali argillosi con acqua sulfurea e salso-bromo-iodica per la preparazione di fanghi peloidi termali e per trattamenti dermatologici. In: Veniale, F. (Ed.), Proc. Symp. "Argille per fanghi peloidi termali e per trattamenti dermatologici e cosmetici", Montecatini Terme/PT, Gruppo Ital. AIPEA. Mineral. Petrogr. Acta, vol. XLII, pp. 267–275.
- Wilson, M.J. (Ed.), 1987. *Handbook of Determinative Methods in Clay Mineralogy*. Blackie, Glasgow.
- Yvon, J., Ferrand, T., 1996. Preparation ex-situ de peloids: proprieties thermiques, mecaniques et d'echange. In: Veniale, F. (Ed.), Proc. Meeting "Argille curative" Salice Terme/PV, Gruppo Ital. AIPEA. Ed. Univ., Pavia, pp. 67–74.