# Muds and salts from Laguna Mar Chiquita (or Mar de Ansenuza), Córdoba, Argentina: natural materials with potential therapeutic uses

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## Abstract

The Laguna Mar Chiquita, located in Cordoba's province, Argentina, is the largest saline lake in South America, with a variable surface between 2,000 to 6,000 km<sup>2</sup>.

During the last 50'and 60' the mud collected directly from the bottom of the lake was extensively used for topical application over the skin and the salts precipitated in the coast were used for domiciliary baths. Subsequent water level increases (decades of the 70, 80, 90) diminish the possibility of using these materials. However, during the last decade the decline of water levels has increased the potential for reuse of muds and salt deposits of this lake.

The aim of this study was to characterize the composition of the muds and salts obtained from Laguna Mar Chiquita like natural materials with potential therapeutic uses.

The salinity of the water, 28 to 360 g/L like minimum and maximum reported, has reached in the last decades values as low as 33 g/L, with salt contents above 70 g/L at the present. The predominant dissolved anion was chloride while sodium was the most important cation. Sulphate was present in minor proportions in the water but it was the most important anion in the precipitated salts. The pH was neutral or slightly alkaline.

The dominant composition of the mud, with possible therapeutic application, was a mixture of illite-like predominant phyllosilicate, quartz, plagioclase, feldspar, muscovite, calcite and halite.

Waters and muds from Laguna Mar Chiquita showed significant similarity to those from the Lo Pagán in Mar Menor, Murcia, Spain, place in which widely promoted tourism is related to the use of muds with therapeutic purposes.

**Key words:** Laguna Mar Chiquita, Muds, Salts

Los lodos y sales de Laguna Mar Chiquita (o Mar de Ansenuza), Córdoba, Argentina: materiales naturales con posibles usos terapéuticos

## Resumen

La Laguna Mar Chiquita, ubicada en la provincia de Córdoba, Argentina, es el mayor lago salino de América del Sur, con una superficie variable entre 2.000 y 6.000 km².

Durante las últimas décadas 50 y 60 el lodo recogido directamente del fondo del lago se utilizaba ampliamente para la aplicación tópica sobre la piel y las sales precipitadas en la costa se utilizaban para baños domiciliarios. Posteriores incrementos del nivel de agua (décadas de los 70, 80, 90) disminuye la posibilidad de utilizar estos materiales. Sin embargo, durante la última década la disminución de los niveles de agua ha incrementado el potencial de reutilización de los lodos y depósitos de sales de este lago.

El objetivo de este estudio fue caracterizar la composición de los lodos y sales obtenidas a partir de Laguna Mar Chiquita como materiales naturales con posibles usos terapéuticos.

La salinidad del agua, de 28 a 360 g/l como mínimo y máximo reportado, se ha alcanzado en los valores de las últimas décadas, como bajo como 33 g / L, con contenidos de sal superiores a 70 g / L en la presente. Los iones disueltos predominantes son el cloruro y el sodio. El sulfato estaba presente en proporciones menores en el agua pero era el anión más importante de las sales precipitadas. El pH era neutro o ligeramente alcalino.

La composición dominante del lodo, con posible aplicación terapéutica, era una mezcla de ilita predominante como filosilicatos, cuarzo, plagioclasa, feldespato, moscovita, calcita y halita

Las aguas y los lodos de la Laguna Mar Chiquita mostrarón una importante similitud con los de la Lo Pagán en el Mar Menor, Murcia, España, lugar relacionado con el turismo que promueva ampliamente la utilización de los lodos con fines terapéuticos.

Palabras clave: Laguna Mar Chiquita, Barros, Sales

## REFERENCE STANDARD

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## INTRODUCTION

There is a long tradition in using fine-grained sediments (muds) for cosmetic and medical purposes. It is well known from historical sources that in several parts of the world muds were used as antiseptic cataplasms to cure skin, stomach and intestinal ailments, as well as for cosmetic purposes<sup>1</sup>.

In modern medicine, the use of healing muds in pharmaceutical formulations, in spas and in aesthetic medicine increased during the last few years due to the increasing interest in and success of natural remedies<sup>2-3</sup>.

The International Society of Medical Hydrology defines "peloid" as "a natural product consisting of a mixture of sea, salt lake, or minero-medicinal water (liquid phase), with organic and inorganic material (solid phase) produced by biological action (humus) and geological action (clay minerals)".

Natural muds obtained from sediments of salt lakes were used in order to cure wounds, soothe irritations, as a method of cleansing the skin, etc. For over 1500 years the general curative powers and therapeutic advantages of the Dead Sea have been well recognized<sup>4</sup>. In Spain the Mar Menor lake, Lo Pagán, is the most important natural saline ecosystem whose sediments are used in therapy<sup>5</sup>.

The Laguna Mar Chiquita, located in Cordoba's province, Argentina, is the largest saline lake in South America, with a variable surface between 2.000 to 6.000 km<sup>2</sup>. Lake level fluctuations are associated to climate changes (dry or wet period) at middles latitudes in south eastern South America<sup>6-7</sup>.

During the last 50' and 60' the mud collected directly from the bottom of the lake was extensively used for topical application over the skin and the salts precipitated in the coast were used for domiciliary baths. Subsequent water level increases (decades of the 70, 80, 90) diminish the possibility of using these materials. However, during the last decade the decline of water levels has increased the potential for reuse of muds and salt deposits of this lake<sup>8</sup>.

The aim of this study was to characterize the composition of the muds and salts obtained from this lake, and compare these materials with that obtained from the Dead Sea and Lo Pagán in Mar Menor.

## **METHODS**

Peloid samples and corresponding mineral water in equilibrium were collected from the Mar Chiquita Lake, Córdoba, Argentina. The temperature, pH and conductivity of each of the disperse systems were measured in situ. The anion and cation contents of the water in equilibrium with the peloid sample were determined in the laboratory using normalised chemical analyses<sup>9</sup>.

The mineralogical composition of the muds was determined by X-ray diffractometry using a Rigaku® Geigerflex and Philips® PW 1710 X-ray diffractometers, with automatic slit, CuK $\alpha$  radiation at 20 mA and 40 kV. Scans were recorded between 2° and 60°(20) with 0.05° step size and 2°/min scanning speed.

## RESULTS AND DISCUSSIONS

# Water phase

The salinity of the water in Mar Chiquita was between 360 to 28 g/L, maximum and minimum reported (years 1911 and 2003 respectively). At the present the salt content in the water is around 70 g/L. Table 1 shows physicochemical parameter measured in water of Mar Chiquita and compared these values with those reported for Dead Sea and Mar Menor

**Table 1 -** Physicochemical parameters of waters of Mar Chiquita, Dead Sea and Mar Menor.

Physicochemical parameter		Mar Chiquita	Dead Sea <sup>10,11</sup>	Mar Menor <sup>5</sup>
pН		7,87	8	8
Conductivity, mS/cm		72,4	131,3	93,4
Total dissolved salts, g/L		69,5	345	78,01
Anions	Cl-, mg/L	32162	239287	41475
	SO <sub>4</sub> <sup>2-</sup> , mg/L	11589	536	6497
	HCO <sub>3</sub> -, mg/L	639	332	122
	CO <sub>3</sub> <sup>2-</sup> , mg/L	63	16	48
Cations	Na+, mg/L	20351	42090	23298
	Ca <sup>2+</sup> , mg/L	3302	18400	391
	Mg <sup>2+</sup> , mg/L	1285	47142	2823
	K+, mg/L	250	8211	1025

The predominant dissolved anion was chloride while sodium was the most important cation in Mar Chiquita system. Sulphate was present in minor proportions in the water but it was the most important anion in the precipitated salts. The pH was neutral or slightly alkaline. Anions and cations concentrations in Mar Chiquita and Lo Pagán, Mar Menor, are very similar.

Waters from Mar Chiquita are, according to the classification of medicinal mineral waters<sup>12</sup>, hyper saline or heavily mineralized, slightly alkaline, chloride, sulphates, sodium and hypo thermals on its average temperature.

The salts dissolved in water were analysed by XRD. This analysis showed a predominance of sodium chloride in the water of the lake.

#### **Solid Phase**

The dominant composition of the peloid (mud) obtained from Mar Chiquita is showed in Table 2, and it is compared with the composition of Dead Sea and Mar Menor muds. The constant in this kind of muds is the presence of salts intercalated with other minerals, specially chloride, sulphates and carbonates.

**Table 2** - Composition of the solid phase of the muds obtained from Mar Chiquita, Dead Sea and Mar Menor.

	$\textbf{Sample} \rightarrow \\ \textbf{Mineral and Chemical composition} \downarrow$	Mar Chiquita	Dead Sea	Mar Menor <sup>5</sup>
Silicates	Quartz: SiO <sub>2</sub>	15	6	9
	Plagioclase: NaAlSi <sub>3</sub> O <sub>8</sub> + CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	15	5	Traces
	Feldspars: KAlSi <sub>3</sub> O <sub>8</sub>	20	5	-
	Mica (Illite, Muscovite): KAl <sub>2</sub> (OH,F) <sub>2</sub> AlSi <sub>3</sub> O <sub>10</sub>	15	-	35
	Kaolinite: Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	-	-	4
	Chlorite: (Fe, Mg, Al)6(Si, Al)4O10(OH)8	-	-	2
Carbonates	Calcite: CaCO <sub>3</sub>	5	35	40
	Dolomite: CaMg(CO <sub>3</sub> ) <sub>2</sub>	-	-	Traces
Chlorides	Halite: NaCl	10	18	6
	Bischofite: MgCl <sub>2</sub> .6H <sub>2</sub> O	-	16	-
	Tachhydrite: CaMg2Cl6.12H2O	-	11	-
Bromides	Magnessium bromide: MgBr2.6H2O	-	Traces	-
Sulphates	Gypsum: CaSO4.2H2O	Variable	2	4
Sulphides	Pyrite: FeS <sub>2</sub>	Variable	-	-
Amorphous		20	2	-

The principal components Mar Chiquita are illite-like predominant phyllosilicate, quartz, plagioclase, feldspar, muscovite, calcite and halite.

Peloids from these salt lakes are characterized by a poverty of clay minerals<sup>5-8-13</sup> unlike the mud used in spas that are generally rich in clay minerals<sup>14</sup>, therefore their therapeutic action is undoubtedly linked to the richness and type (variety) in salts.

The salts cations can penetrated and inserted into the structure of the clay minerals. Thus, the therapeutic effects can be associated with two mechanisms: the

presence of the salts themselves and the changes suffered by the clay minerals when the salts ions are intercalated inside them<sup>8-15</sup>.

Waters and muds from Laguna Mar Chiquita showed significant similarity to those from Lo Pagán, Mar Menor, Murcia, Spain<sup>5</sup>.

#### CONCLUSIONS

Water, salts and muds found in Mar Chiquita, Córdoba, Argentina, are compounds commonly used for therapeutic purposes.

Chemical and mineralogical composition of this system is very similar to that found in Lo Pagán, Mar Menor, and the two systems are similar in nature to the Dead Sea.

Muds of these salt lakes are characterized by their low presence of clay minerals in contrast to the muds used in spas, either natural or prepared in situ, while it is remarkable the presence of salts.

The therapeutic effects of these materials are undoubtedly associated with the presence and type of salts found in these ecosystems.

## REFERENCES

- 1. Carretero MI, Pozo M. Clay and non-clay minerals in the pharmaceutical industry Part I. Excipients and medical applications. Appl Clay Sci. 2009; 46:73-80.
- López-Galindo A, Viseras C. Pharmaceutical and cosmetic applications of clays, in: Clay Surfaces, Fundamentals and applications, Interface Science and Technology, Wypych and Gundappa Satyanarayana Eds. Elsevier. 2004, 267-289.
- 3. Veniale F, Bettero A, Jobstraibizer PG, Setti M. Thermal muds: Perspectives of innovations. Appl Clay Sci. 2007; 36:141-147.
- 4. Nissenbaum A. Ancient and Modern medicinal applications of Dead Sea asphalt (bitumen). Israel Journal of the Earth Sciences. 1999; 48:301-8.
- 5. Carretero MI, Pozo M, Martin-Rubi JA, Pozo E, Maraver F. Mobility of elements in interaction between artificial sweat and peloids used in Spanish spa. Appl Clay Sci. 2010; 48:506-515.
- 6. Piovano E, Ariztegui D, Damatto S. Recent environmental changes in Laguna Mar Chiquita (central Argentina): a sedimentary model for a highly variable saline lake. Sedimentology. 2002; 49:1371-1384.
- 7. Troin M, Vallet-Coulomb C, Sylvestre F, Piovano E. Hydrological modelling of a closed lake (Laguna Mar Chiquita, Argentina) in the context of 20th century climatic changes. Journal of Hydrology. 2010; 393:233-244.

- 8. Baschini M, Piovano E, Setti M. Aguas, Fangos y sales naturales con Potenciales Usos terapéuticos, Laguna Mar Chiquita Córdoba Argentina. Editorial Educo, 2011, 62 pp.
- 9. APHA, AWWA, WPCF. Standard Methods for the Examination of Water and Wastewater, 17 ed. American Public Health Associations, Washington, 1989: 1.5–3.12.
- 10. Momani K, El-Hasan T, Auaydeh S, Al-Nawayseh K. Heavy Metals Distribution in the Dead Sea Black Mud. Jordan Journal of Earth and Environmental Sciences. 2009; 2:50-59.
- 11. Tamimia A, Rawajfeh K. Lumped modeling of solar-evaporative ponds charged from the water of the Dead Sea. Desalination. 2007; 216:356–366.
- 12. Armijo Valenzuela M, San Martín Bacaicoa J. Curas Balnearias y Climáticas. Ed. Complutense, 1994.
- 13. Khlaifat A, Al-Khashman O, Qutob H. Physical and chemical characterization of Dead Sea mud. Material Characterization. 2010; 61:564-568.
- Baschini MT, Pettinari GR, Vallés JM, Aguzzi C, Cerezo P, López-Galindo A, Setti M, Viseras C. Suitability of natural sulphur-rich muds from Copahue (Argentina) for use as semisolid health care products. Appl Clay Sci. 2010; 49:205-212.
- 15. De Michele D, Giacomino M, Untura-Filho M, Beldarrain A. Efectos sistémicos de los fangos minerales. Revisión de la literatura de los últimos 10 años. Balnea. 2008; 4:115-122.