Revista de Investigación de Física **23(1)**, (Ene-Jun 2020)
eISSN:1728-2977

An updated study of the magnetic fraction in medicinal sediments from two Peruvian lagoons

María Luisa Cerón L.*[1,2], Jorge Bravo[1], Franko Urcia [3], Martin Salazar [3] y Felipe Reyes [1]

[1] *Universidad Nacional Mayor de San Marcos, Lima, Perú*
[2] *Universidad Cesar Vallejo, Lima, Perú*
[3] *Universidad Nacional Pedro Ruíz Gallo, Lambayeque, Perú*

Recibido 30 noviembre 2019 – Aceptado 31 enero 2020

Abstract
We studied diverse minerals found in the magnetic fraction of clays from medicinal sediments collected in two Peruvian lagoons, La Milagrosa (MML) and La Mellicera (MELL). The clay fraction was separated by the sedimentation method. The analytical physical techniques we used were energy dispersive X-ray fluorescence (EDXRF), X-ray diffractometry (XRD) and transmission Mössbauer spectroscopy (TMS). We complemented them with a physical chemical analysis to determine texture, pH and electrical conductivity. We have observed, via XRD, minerals such as illite, calcite and maghemite. Specifically, for MML, by XRD we observed two minerals phases: quartz and dolomite. TMS allowed us to observe the magnetic fraction of the sediments. In the spectra we observed four magnetic sextets and three paramagnetic doublets. The sextets were assigned to hematite/goethite, two sites of magnetite (Fe^{3+} and $Fe^{2.5+}$) and maghemite. Likewise, the doublets were assigned to Fe^{2+} and Fe^{+3}, sites assigned to illite and pyrite, respectively.

Keywords: energy dispersive X-ray fluorescence, X-ray diffractometry, transmission Mössbauer spectroscopy.

Un estudio actualizado de la fracción magnética en sedimentos medicinales provenientes de dos lagunas Peruanas

Resumen
Estudiamos diversos minerales encontrados en la fracción magnética de arcillas de sedimentos medicinales recolectados en dos lagunas peruanas, La Milagrosa (MML) y La Mellicera (MELL). La fracción de arcilla se separó por el método de sedimentación. Las técnicas analíticas físicas que utilizamos fueron la fluorescencia de rayos X por energía dispersiva (FRXED), la difractometría de rayos X (DRX) y la espectroscopía Mössbauer de transmisión (EMT). Éstas técnicas las complementamos con un análisis físico-químico para determinar la textura, pH y conductividad eléctrica de las muestras recolectadas. Así, hemos observado, a través de DRX, minerales como ilita, calcita y maghemita. Específicamente, para MML, por DRX observamos dos fases minerales: cuarzo y dolomita. La EMT nos permitió observar la fracción magnética de los sedimentos. En los espectros observamos cuatro sextetos magnéticos y tres dobletes paramagnéticos. Los sextetos fueron asignados a hematita/goethita, dos sitios de magnetita (Fe^{3+} y $Fe^{2.5+}$) y maghemita. Asimismo, los dobletes se asignaron a Fe^{2+} y Fe^{+3}, sitios asignados a ilita y pirita, respectivamente.

Palabras clave: fluorescencia de rayos X por energía dispersiva, difractometría de rayos X, espectroscopía de transmisión Mössbauer.

*mceronl@unmsm.edu.pe

Introduction

The study of the mineral-medicinal lagoons is important, since it is necessary to know if people put their health at risk by immersing themselves in these types of lagoons (Cerón et al. 2015 [Cer15], Pérez & Segarte 2001 [Per01], Furet et al. 1996a [Fur96], Furet et al. 1996b [Fur96b], Herrera et al. 1996 [Her96]). In this work, we present updated results on the study of two mineral-medicinal effluents named 1) La Milagrosa (MML) with GPS-coordinates 12° 32′ 40.7328″ S and 76° 43′ 24.0528″ W, and 2) La Mellicera (MELL) with GPS-coordinates 12° 32′ 34.8504″ S and 76° 43′ 31.0044″ W. Both of them are located in the Chilca District, Cañete Province, Lima Region, Perú.

The results of an earlier study (Cerón et al. 2015) [Cer15] show variations with respect to the results of much earlier studies: such as pH, (Cerón et al. 2005a, 2005b [Cer05]). Thus, herein, we introduce an updated study. In the two lagoons, the depth has not changed. The samples were collected in situ with an extractor that allowed obtaining samples at different depths and extraction points (Figure 1a). The extracted samples present different characteristic colors, texture and composition. These samples were called MML-VER, MML-CR, MML-PCL and MML-NEG, all extracted from the central part of the lagoon, except MML-EXT, extracted from the end of the lagoon (Figure 1b). The first extraction was made in a warmer season at high temperatures ($\sim$ 23°C to 28°C); the second extraction was made in May, when the weather is colder ($\sim$ 15°C to 18°C).

The results we obtained correspond to the sand fraction (<2 mm particle diameter), clay fraction (<2 μm particle diameter) and the magnetic fraction.

Finally, since the magnetic phases are frequently not detected with analytical techniques (such as XRD, due to their low concentrations), we have used TMS, an isotopically selective technique, which made possible to identify the magnetic minerals contained in the corresponding sample. The microbiological and pharmacological studies to complete the results have not yet been completed.

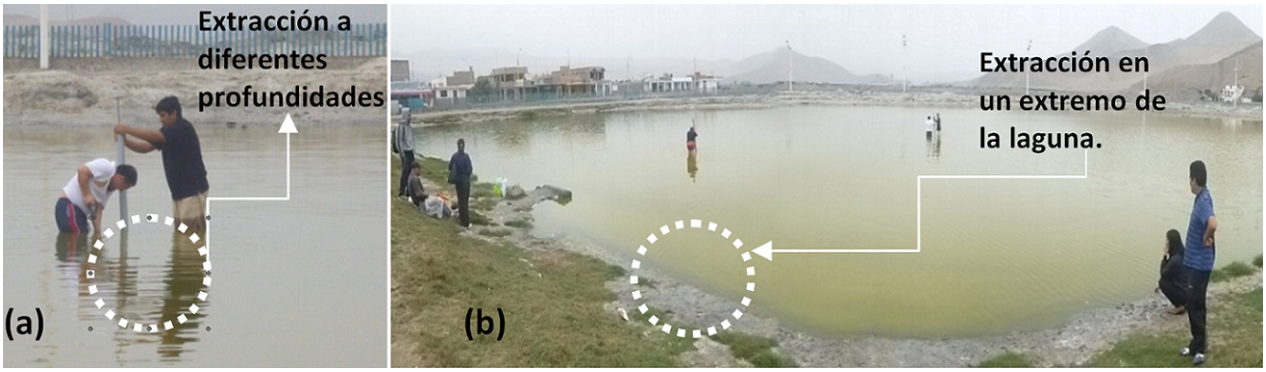

Figure 1: In situ extraction of the samples from the lagoons by using an extractor.

Samples	Code	Characteristic	Depth	Color
La Milagrosa (MML)	MML- CR	Has organic matter.Extracted from the central part of the lagoon.	$\sim$ 40 cm	cream
	MML- VER	Has organic matter.Extracted from the central part of the lagoon.	$\sim$ 40 cm	greenish
	MML- NEG	Has organic matter.Extracted from the central part of the lagoon.	$\sim$ 40 cm	blackish
	MML- PCL	Has organic matter.Extracted from the central part of the lagoon.	$\sim$ 10 cm	leaden
	MML- EXT	Has organic matter.Extracted from the central part of the lagoon.	$\sim$ 10 cm	leaden
La Mellicera (MELL)	MELL	Has organic matter.Extracted from the central part of the lagoon.	$\sim$ 10 cm	blackish

Table 1: Samples Analyzed.

Materials and Methods

After the corresponding extraction, the samples were taken to the Laboratory of Soil Analysis of the Faculty of Physical Sciences (UNMSM). Now, we must indicate that we called MML-EXT5 the MML sample extracted in 2014. In Table 1 we have the primary identification of the samples with their respective characteristics.

Preparation of the samples

The samples were prepared in the Soil Analysis Laboratory, dried at room temperature (∼22°C), then grounded with a mortar and, afterwards, sieved to obtain the different granulometric fractions, that is, sand-, silt-, and clay-size fractions. This last fraction was obtained by the sedimentation method (Figure 2), which delayed approximately 2 weeks for each sample (Manual de Laboratorio de Análisis de Suelos, UNMSM (2000) [Bra00]). Likewise, the procedure had to be repeated, in order to obtain more samples and continue with the analysis. Besides, the magnetic part was extracted using a routine technique; specifically, using a magnetic stirrer and some magnets, for samples MML-EXT-MAG and MELL-MAG.

Physical-chemical measurements

Measurement of the degree of alkalinity

The preparation of the samples for the pH analysis was carried out by following the Soil Laboratory Manual of the Faculty of Physical Sciences of the UNMSM. We used a pHTester BNC/OAKTON instrument, model 35624-10 (Table 2).

Figure 2: Instruments used to obtain the clay fraction by the sedimentation method.

Measurement of electrical conductivity

To measure the electrical conductivity, it was necessary to prepare a saturated paste and extract it through a pressure filter, that is, by using a vacuum pump. This way, we obtained an extract that was subjected to measurement with a conductivity meter. This allowed us to estimate an approximate quantitative amount of salts contained in the samples (Table 3).

Samples	pH (in the Lab)	Temperature of the liquid (°C)
MML-CR	8.6	20.9
MML-VER	8.7	20.0
MML-NEG	8.5	21.3
MML-PCL	9.3	21.3
MML-EXT	9.8	22.1
MELL	9.9	22.3

Table 2: pH and temperature obtained from the samples

Physical Techniques Applied

Energy Dispersive X-ray Fluorescence (EDXRF)

The analysis of the elemental composition was carried out in two different stages by using EDXRF (Jenkins 2012) [Jen12]. Concerning the first one, for MML-EXT5, the results of Table 4 were obtained with the support of the EDXRF team of Dr. Paula Olivera in the Peruvian Institute for the Nuclear Energy (IPEN is its Spanish acronym). Concerning the second one, Table 5 shows updated results obtained by using a portable EDXRF equipment brand, which uses an X-rays tube with a silver target. This tube operates at 30 kV and 50 μA. EDXRF allowed us to recognize chemical elements having Z>12 (greater than magnesium). Thus, the elemental composition, qualitative and quantitative, was determined. The uncertainty in the measurement of the concentrations was 10% approximately.

Samples	Elect. cond. (μS)	Temperature of the liquid (°C)
MML-CR	182.7	21.6
MML-VER	1388	18.8
MML-NEG	1415	18.7
MML-PCL	1180	20.0
MML-EXT	1577	18.9
MELL	1356	19.3

Table 3: Electrical conductivity of the samples.

Percentage of metal	MML-EXT5
K (%)	< 3
Ca (%)	31± 1
Fe (%)	3.23±0.05
Co (ppm)	447±85
Cu (ppm)	1515±40
Zn (ppm)	150±19
As (ppm)	< 134
Sr (ppm)	4664±75
Zr (ppm)	101±7
Y (ppm)	< 7
Pb (ppm)	205±17

Table 4: Quantitative analysis by EDXRF of the MML-EXT5 sample extracted in 2014, in percentage by mass

X-ray diffractometry (XRD)

We used this technique to make a structural analysis of the minerals present in the sample (Lipson 1970 [Lip70], Cullity 2001 [Cul01]). Specifically, for MML-EXT5, we used a MINIFLEX RIGAKU diffractometer, which uses radiation from Cu-Kα (λ=1.54178 Å). For MML-EXT and MELL, we used a Bruker diffractometer, model D8-Focus, with a Cu-Kα radiation (λ=1.54178 Å). The two diffractometers operated at 40 kV and 40 mA in a vertical goniometer; the range of the angle scale was $4^\circ<2\theta<70^\circ$ and the 2θ advance was 0.02°/step with an interval of 3 s per step.

^{57}Fe transmission Mössbauer spectroscopy (TMS)

This technique was used to obtain detailed information about minerals that contain iron (Yoshida and Langouche 2013 [Yos13], Stevens et al. 2005 [Ste05]). We used a conventional Mössbauer spectrometer with a sinusoidal velocity modulation signal and 1024 channels. The Mössbauer spectra were taken at room temperature ($\sim$ 298 K) in a transmission geometry using a ^{57}Co source in a rhodium matrix. These spectra were analyzed by using the Normos program, created by Richard Brand in 1995, at the Archeometry Laboratory of the Faculty of Physical Sciences of the UNMSM.

Elements	Samples			
	MML-EXT	MML-PCL	MML-VER	MML-CR
Al	0.0002	15.1734	0.0002	0.0002
Si	11.3744	2.2006	0.00	0.00
P	0.00	0.00	0.00	0.00
S	0.6520	1.9491	1.2551	0.70
Cl	1.9103	10.0932	3.9749	3.2212
K	1.2964	1.5761	1.5663	1.7859
Ca	4.7555	8.8050	11.8307	14.0876
Ti	0.1670	0.0572	0.00	0.0503
V	0.00	0.00	0.00	0.00
Cr	0.0092	0.0107	0.00	0.00
Mn	0.0866	0.0477	0.0171	0.0452
Fe	1.8213	1.2055	0.4364	1.0209
Co	0.0342	0.0199	0.0303	0.0583
Ni	0.00	0.00	0.0017	0.00
Cu	0.0037	0.0014	0.0049	0.0052
Zn	0.0112	0.0096	0.0097	0.0098
Br	0.0028	0.0233	0.0051	0.0044
Rb	0.00	0.00	0.00	0.00
Sr	0.0988	0.2858	0.2788	0.4423
Zr	0.0045	0.0070	0.0155	0.0133

Table 5: Updated quantitative analysis by EDXRF of the different samples, in percentage by mass.

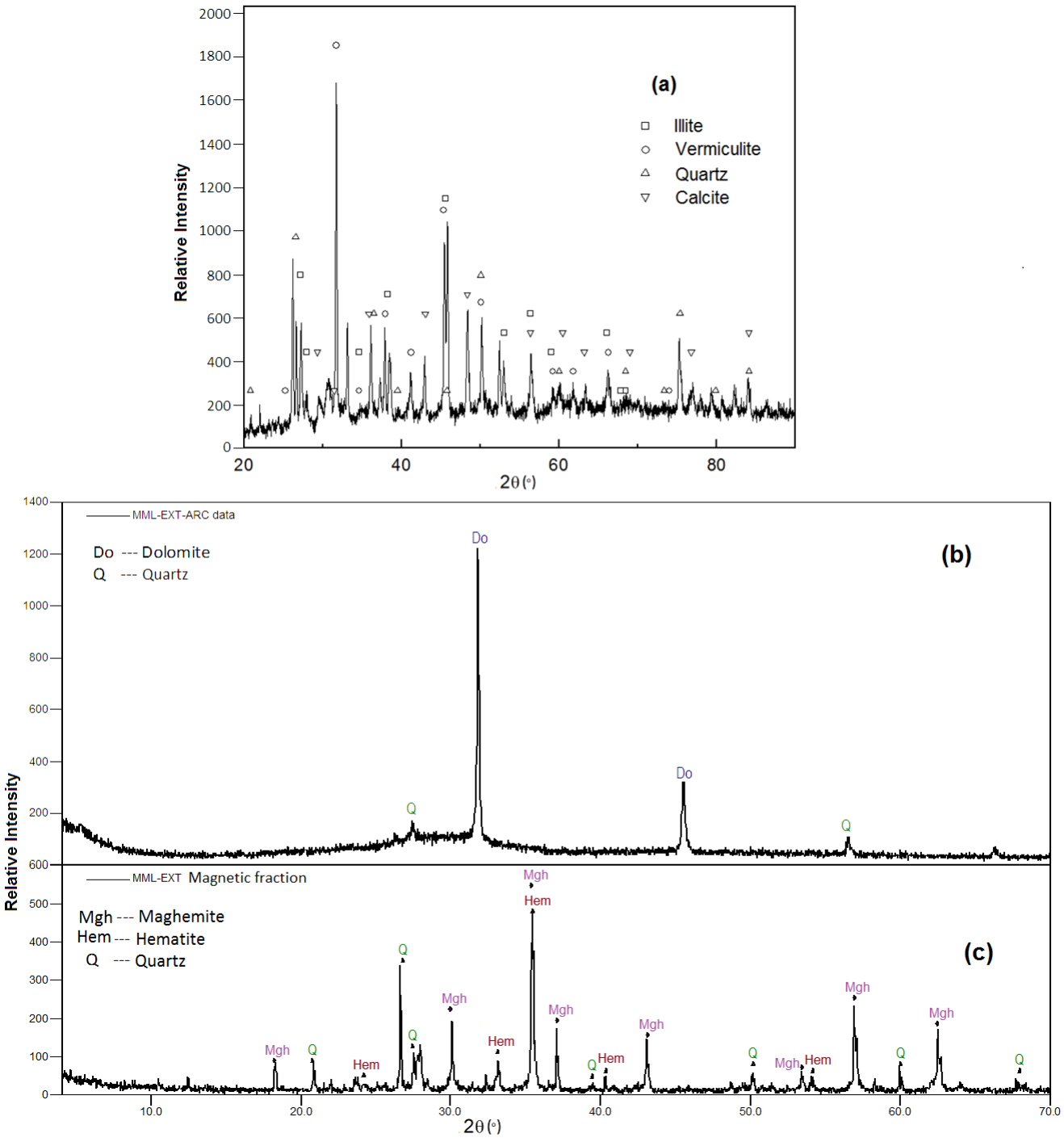

Figure 3: (a) X-ray diffractogram of the MML-EXT5 sample extracted in 2014. X-ray diffractogram of the MML-EXT sample corresponding to (b) the clay fraction and (c) the magnetic fraction.

Results and Discussions

Physical-chemical analysis

Table 2 shows the obtained results concerning the degree of alkalinity of the samples. Table 3 shows the corresponding conductivity results. All these values were recorded both in situ in extracting the samples and ex situ in the soils analysis Laboratory after three days. All samples have a high degree of alkalinity; this is due to the high concentration of basic ions present in the samples.

Energy dispersive X-ray fluorescence (EDXRF)

In Table 5 we observe the following: the major percentage of Al is presented by the MML-PCL sample; for Si, it is noticed that MML-EXT>MML-PCL; for S, we have MML-PCL>MML-VER>MML-CR>MML-EXT; for Cl, we observe that the MML-PCL sample has the major percentage when it is compared with the all other samples; K is invariable. Also, concerning Ca, we have MML-CR>MML-VER>MML-PCL>MML-EXT; concerning Fe, we have MML-EXT>MML-PCL>MML-CR>MML-VER. Besides, the MML-EXT sample has more concentration of Si and Fe, whereas the MML-PCL sample has more concentration of S and Cl followed by Fe and Si. These last samples are the most representative of La Milagrosa lagoon.

X-ray diffractometry

In all the diffractograms shown in Figure 3, the presence of quartz (SiO4) is observed in the samples; it is a primary mineral difficult to dissolve. In Figure 3 a, we observe the results for the clay fraction in MML-EXT5, where the additional structural phases illite, vermiculite and calcite are registered. In Figure 3 b, for the MML-AR-EXT sample, we observe one structural phase, dolomite [$CaMg(CO_3)_2$], which is observed with its main peaks. In Figure 3 c, for the magnetic fraction of MML-EXT-MAG, we observe the structural phases of hematite (Hem) and maghemite (Mgh); it is also noticed the superimposed main peaks of Hem + Mgh, well defined at $2\theta = 35.5°$, and the primary mineral quartz.

Transmission Mössbauer spectroscopy (TMS)

In Figure 4, we observe the Mössbauer spectra for the MELL samples. In Figure 4a, for MELL-AR, we have the clay fraction Mössbauer spectrum recorded at speed v = 11 mm/s. In this spectrum, with an absorption percentage of 7%, we observe a unique magnetic sextet S1 assigned to goethite and three paramagnetic doblets D1, D2 and D3. Doblets D1 and D2 were assigned to sites Fe^{3+} and Fe^{+2}, both corresponding to illite. Doblet D3 was assigned to the Fe^{3+} site, corresponding to pyrite.

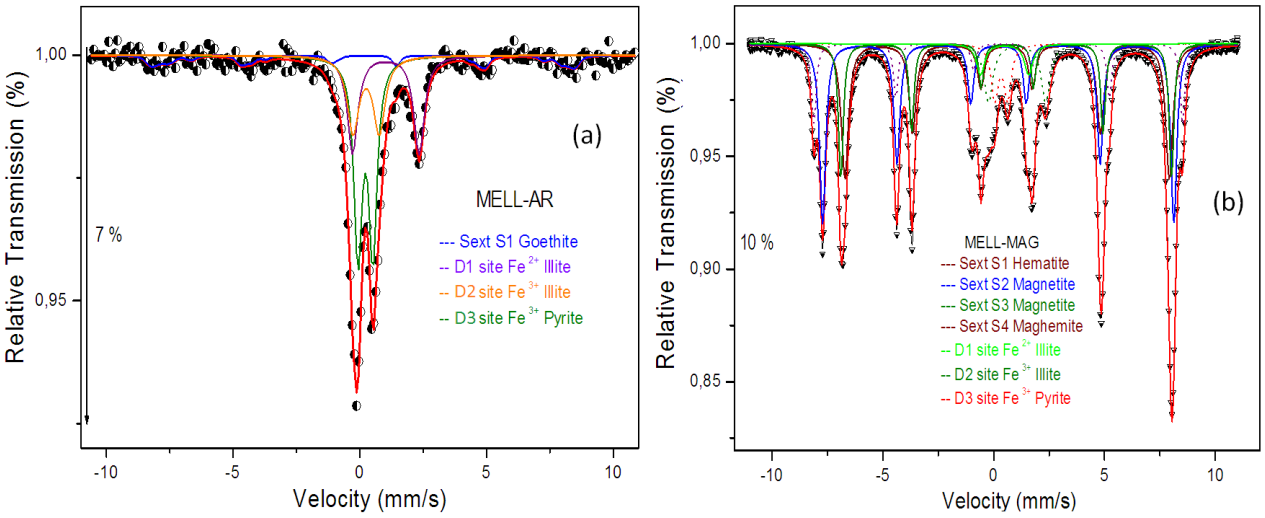

Figure 4: TSM spectrum of the MELL sample recorded at v = 11 mm/s (a) MELL-AR, clay fraction, and (b) MELL-MAG, magnetic fraction.

In Figure 4b, for MELL-MAG, with an absorption percentage of 10%, we have the TMS spectrum for the magnetic fraction. The mineralogical composition was attributed to the presence of four magnetic sextets (S1, S2, S3 and S4) and three magnetic doblets (D1, D2 and D3). Sextet S1 was assigned to hematite/goethite. Sextet S2 and sextet S3 were assigned to magnetite (Mag), these sextets are partially resolved on the tetrahedral sites (site A, Fe^{+3}), with B_{hf}=49.53 T and the octahedral sites (sites B, $Fe^{+2.5}$ due to Fe^{3+} and Fe^{2+}), with B_{hf}=46.72 T. The population of iron on the octahedral site is approximately two times the corresponding to the tetrahedral site; this is observed in Table 6 (where we have the areas). Sextet S4 was assigned to maghemite (Mgh). Concerning to the doblets, D1 and D2 correspond to the Fe^{+2} and Fe^{+3} sites assigned to illite, and D3 corresponds to Fe^{+3} assigned to pyrite.

In Figure 5, we observed the MML-EXT TMS spectra. In Figure 5a, we have the clay fraction spectrum recorded at low speed, v = 2 mm/s; with an absorption percentage of 0.5%, we observed one paramagnetic doublet corresponding to one site Fe^{+3} assigned to the dolomite.

In Figure 5b, with an absorption percentage of 20%, we have the magnetic fraction, whose mineralogical composition is attributed to the presence of four magnetic sextets S1, S2, S3 and S4. These ones were interpreted thus: sextet S1 is hematite; S2, the tetrahedral magnetite contribution; and S3 and S4 combined, the octahedral magnetite contribution. This is because when the magnetite is impure or poorly crystalline, it always has the octahedral contribution broadened. Likewise, we observed three paramagnetic doublets D1, D2 and D3. Doublets D1 and D2 correspond to the Fe^{+2} and Fe^{+3} sites assigned to illite; doublet D3 corresponds to the Fe+3 site assigned to pyrite.

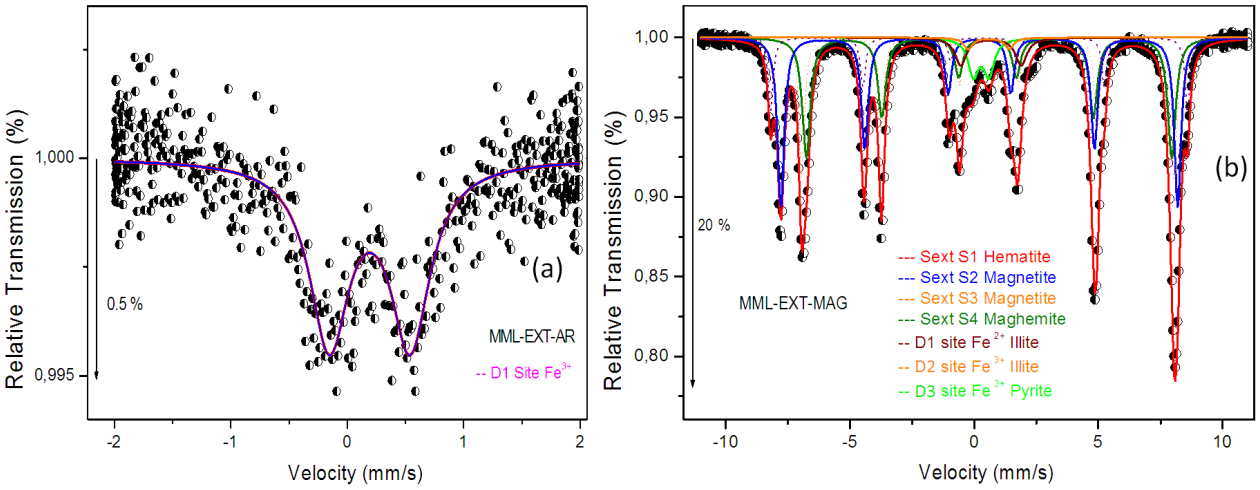

Figure 5: Transmission Mössbauer spectrum of the MML sample. (a) Clay fraction recorded at v = 2 mm/s, and (b) magnetic fraction at v = 11 mm/s.

We realized the magnetic composition of MELL-MAG and MML-EXT-MAG did not change even though these samples were registered in different extraction points. This must be because they are samples from neighboring lagoons.

For MML-EX-AR, by XRD we observed the presence of dolomite and by TMS we do not observe this mineral; however, this does not imply that this mineral is not present in the sample. That is, we know that TMS is a selective isotopically technique, which allows us to observe minerals having too little Fe, and we know that dolomite has Ca and Mg in its structure; it is probable that an ion exchange of Mg and Fe has not happened. Likewise, by TMS we observed the presence of one paramagnetic doblet corresponding to pyrite, which is not observed by XRD because it has less than 5% of Fe present in the sample.

Likewise, Table 6 shows the Mössbauer parameters of the MML and MELL samples, clay and magnetic fractions. In this table, δ stands for the isomer shift ε, the quadrupole shift ΔE_Q, the quadrupole splitting; B_{hf} is the hyperfine field; A, the spectral area; and Γ, line width.

Conclusions

In the studied mineral-medicinal effluents, we registered a high degree of alkalinity, this due to the presence of a high concentration of basic ions. The elemental composi-

tion shows more concentration for Si and Fe, followed by S and Cl. The dominant clays would have in its structure sites of Fe^{+2} and Fe^{+3}, corresponding to illite.

The mineralogy of the magnetic fraction was obtained for both set of samples studied; their respective magnetic composition did not change; it was the same even when we had registered samples from different extraction points. The reason for this is due to the samples from the same lagoon. This magnetic composition corresponds to sites of Fe^{+3} and Fe^{+2} oxides assigned to hematite and magnetite.

Likewise, we suggest complementing these studies in an interdisciplinary way, with researchers from the biological and medical areas, to give more precise results and authorize if people can dive into the lagoons without risking their health.

Sites	Parameters	Samples			
		MML-EXT-AR	MML-EXT-MAG	MELL-AR	MELL-MAG
Sextet S1 hematite/goethite	$\delta(mm/s)$		0.286	0.33	0.286
	$\frac{2\varepsilon}{\Delta E_Q}$		-0.221	-0.10	-0.221
	$B_{hf}(T)$		51.88	41.0	51.88
	$A(\%)$		10.302	88.31	10.56
	$\Gamma(mm/s)$		0.21	0.31	0.26
Sextet S2 magnetite sites B, Fe^{+3}	$\delta(mm/s)$		0.211(4)		0.21
	$\frac{2\varepsilon}{\Delta E_Q}$		-0.021(7)		-0.021
	$B_{hf}(T)$		49.53(4)		49.53
	$A(\%)$		31.41		29.68
	$\Gamma(mm/s)$		0.328		0.33
Sextet S3 magnetite sites B, $Fe^{+2.5}$	$\delta(mm/s)$		0.587		0.59
	$\frac{2\varepsilon}{\Delta E_Q}$		-0.073		-0.073
	$B_{hf}(T)$		46.72		46.72
	$A(\%)$		20.81		17.50
	$\Gamma(mm/s)$		0.258		0.258
Sextet S4 maghemite	$\delta(mm/s)$		0.541(1)		0.35
	$\frac{2\varepsilon}{\Delta E_Q}$		0.056(1)		0.028
	$B_{hf}(T)$		45.86()		45.36
	$A(\%)$		26.40		26.37
	$\Gamma(mm/s)$		0.39		0.39
D1 illite Fe^{2+}	$\delta(mm/s)$		1.01	1.026	0.60
	ΔE_Q		2.44	2.63	2.1
	$A(\%)$		4.38	25.97	7.1
	$\Gamma(mm/s)$		0.56	0.50	0.48
D2 illite Fe^{3+}	$\delta(mm/s)$		0.11	0.226	0.40
	ΔE_Q		1.34	1.14	2.78
	$A(\%)$		1.46	22.13	3.54
	$\Gamma(mm/s)$		0.44	0.55	0.45
D2 pyrite Fe^{3+}	$\delta(mm/s)$	0.192	0.164	0.22	0.201
	ΔE_Q	0.714	0.88	0.62	0.66
	$A(\%)$	100.0	5.24	40.22	5.27
	$\Gamma(mm/s)$	0.412	0.51	0.384	0.38

Table 6: Mössbauer parameters of the MML and MELL samples, clay and magnetic fractions.

Acknowledgements

We are grateful to the anonymous reviewers for their comments and suggestions. We acknowledge the contribution of the Laboratories of Analysis of Soils, Archaeometry, and X-Ray Diffractometry at Universidad Nacional Mayor de San Marcos.

References

[Bra00] Bravo C., Jorge A. (2000). Manual de Laboratorio de Análisis de Suelos. Laboratorio de Análisis de Suelos. Facultad de Ciencias Físicas. UNMSM.

[Cer05] Cerón, M., Furet, N., Bustamante, A., Quispe, J., Bravo, J. y Trujillo, A. (2005). Caracterización mineralógica de los peloides de las salinas de Chilca (Mineralogical characterization of the peloids of the Chilca salinas). Revista de Investigación de Física, vol. 8(2), pp 9-13.

[Cero05] Cerón, M., Furet, N., Bustamante, A., Quispe, J., Bravo, J. and Trujillo, A. (2005). Characterization mineralogical of the peloid "La Mellicera" by Mossbauer Spectroscopy, X-Ray Diffraction and Scanning Electron Microscopy, Conference Proceedings T4-P18 - ICAME 2005, Montpellier, France.

[Cer15] Cerón, M., Bravo, J., Navarro, F., Urcia, F. (2015). Updated Mineralogical Analysis of Sediment Materials from Three Therapeutically-used Peruvian Lagoons. Journal of Metals, Materials and Minerals. 25 (1), pp 61-67.

[Cul01] Cullity, B. and Stock, S. (2001). Elements of X-Ray Diffraction, third edition, USA: Pearson.

[Fur96] Furet, N., Rodríguez, A., Quinteros, M., Portilla, C. (1996). Evaluación química de peloides de varias salinas de Cuba (Chemical evaluation of peloids from several salinas of Cuba). Contribuciones a la Hidrología y Medio Ambiente en Cuba. 349-356.

[Fur96b] Furet, N., Rodríguez, A., Portilla, C., Díaz, A., Luna, B., Moya, N.M. (1996). Los Peloides de las salinas Bidos (The Peloides of the Bidos Salinas). Un estudio por espectroscopia Mössbauer del 57Fe y Espectrometría de Absorción Atómica (A study by Mössbauer spectroscopy of 57Fe and Atomic Absorption Spectrometry). Contribuciones a la Hidrología y Medio Ambiente en Cuba. 341-347.

[Her96] Herrera, I., Rodríguez, A., Toledo, C., Furet, N., Cañizares, H. (1996). Caracterización químico estructural de fangos medicinales (Structural-chemical characterization of medicinal sludge). Contribuciones a la Hidrología y Medio Ambiente en Cuba. 325-339.

[Jen12] Jenkins, R. (2012). X-Ray Fluorescence Spectrometry, Vol. 152, 2nd edition, New Jersey: John Wiley & Sons.

[Lip70] Lipson, H. (1970). Crystals and X-rays, London: Wykeham Publications (Science Series).

[Per01] Pérez, M., Segarte, F. (2001). Utilización de Recursos Termales en la Búsqueda de Salud y Belleza (Utilization of Thermal Resources in the Search for Health and Beauty). Rev. Cubana Farm. 35(3), pp 207-211.

[Ste05] Stevens, J.G., Khasanov, A.M., Miller, J.W., Pollak, H., Li, Z. (Eds): (2005). Mössbauer Mineral Handbook, Asheville: Mössbauer Effect Data Center.

[Yos13] Yoshida, Y., Langouche G. (Eds.): (2013). Mössbauer Spectroscopy, Germany: Springer-Verlag Berlin Heidelberg.