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PIXE Based Geochemical Characterization of the Pluvial Lake Palomas System, Chihuahua Mexico

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Abstract. The Pluvial Lake Palomas System is located in the Chihuahuan Desert in northern Chihuahua, Mexico. This Pleistocene lake (12 -15 ka) inundated a surface close to 7,800 km^2 during the last glacial age. Pluvial Lake Palomas is presently composed of several perennial open and closed hydrologic basins. In the Mexican side these basins include: The Bolson de los Muertos (largest), Laguna Santa Maria, Laguna el Fresnal, Laguna Guzman and Lake Palomas. Areas in the US side include the Indian Basin of Luna County, New Mexico. Mineral aerosols emplaced from these basins are responsible for constant air quality violations in northern Chihuahua, western Texas and far beyond, making it one of the principal sources of aeolian sediments in the Chihuahuan Desert. The sediment load deposited in these basins range from gravel and sand size sediments at the basins shorelines, to mixtures of finer silt, clay and sand particles towards the center of the basins. Pluvial Lake Palomas was originally inundated by the ancestral Rio Grande/Bravo, suggesting a semi-homogeneous sediment chemical composition. Later in time the Mimbres River joined the Rio Grande/Bravo in the inundation of the system. At present time the system (as individual basins) is inundated by the perennial Casas Grandes River (NW), the Santa Maria River (SW) and the Del Carmen River (S–SW). The input from these rivers and the presence of the flanking ranges contribute to create a distinct chemical composition of each basin's sediments in the system. Each basin is geochemically characterized using elemental compositions of lacustrine sediment samples determined by PIXE analysis. The resulting geochemical signatures will provide comparison parameters to aerosol samples collected downwind in northern Chihuahua, Southwest Texas and possibly as far as Canada.

Keywords: PIXE, Pluvial Lake Palomas, Cluster Analysis, Elemental Concentrations, Mineral Aerosols.

INTRODUCTION

The Pluvial Lake Palomas (PLP) System is located in the Chihuahuan Desert across the Mexico-USA international border. At its maximum climatic point (12 -15 ka before present) PLP inundated a surface close to 7800 km^2. PLP encompasses a surface elongated in a N-S direction for close to 200 km in length, and average of 25 km width. Presently Pluvial Lake Palomas is subdivided into several perennial open and closed hydrologic basins. The Bolson de Los Muertos (largest of them), Laguna Santa Maria, Laguna El Fresnal, Laguna Guzman and Lake Palomas are on the Mexican side, and the Indian Basin of New Mexico on the USA side. When these basins inundate during the rainy season, standing water can be retained at the surface for periods ranging from weeks to months. The year 2006 marked a ≥100 year pluvial return period characterized by abundant and frequent rain events which caused the majority of these basins to inundate. Almost 1 year after the rains some of the playa surfaces still retained water. These inundations caused the shorelines of some basins to extend almost a kilometer landward and to inundate areas that had not been previously inundated due to the prolonged (9-10 year) drought that the region had experienced. This phenomenon altered the morphology of these playas, both surface texture and spatial extent. Most playas experienced a sediment load recharge, and all surfaces experienced a textural reset.

The sediment load deposited in these basins ranges from gravel and sand size sediments at the shorelines, to mixtures of finer silt, clay and sand particles towards the center of the basins. At the playas surfaces the sediments are gradationally deposited leaving the finer materials clay and silt fraction (PM 2.5, PM 10 and larger) at the surface. When these sediments dry they become prone to wind erosion and transport. These sediments are commonly emplaced as mineral aerosols into the atmosphere. Mineral aerosols emplaced from these basins are responsible for constant air quality violations in northern Chihuahua, western Texas and far beyond, making it one of the principal sources of aeolian sediments in the Chihuahuan Desert (1).

The multi-fluvial input to the basins of Pluvial Lake Palomas along with the presence of geologically diverse flanking ranges (e.g. carbonates, sedimentary clastics and varied igneous lithologies), some of them with key mineral assemblages, could contribute to create a distinct chemical composition of each basin's sediments in the system. Each basin is geochemically characterized using elemental compositions of lacustrine sediment samples determined by PIXE analysis. The resulting geochemical signatures will provide comparison parameters to aerosol samples collected downwind.

SAMPLING AND ANALYSIS

A total of 25 lacustrine sediment samples were collected and analyzed from the Pluvial Lake Palomas (PLP) basins. Multiple samples were collected in all individual basins. Some of the samples represent diverse areas of each individual basin. Furthermore some samples were collected from one year to the next, before and after the rainy season (most samples collected in 2006 except where noted). Three samples were collected in a basin apparently located outside the PLP. These samples are included because the basin (Ascension basin) has been identified as a main mineral aerosol source (Table 1).

TABLE 1. Samples Index by basins.

Basin	Sample	Remarks
Bolson de los Muertos	CLP001, CLP002, SELP003, SELP005, SELPTB, GV001, GV002, HWY2-001, COR005, COR006	CLP and COR samples are from the central area of the playa. SELP from the southeast area. GV and HWY2 area from the northern area.
Laguna el Fresnal	LF001top, LF001bottom, LF001flakes, LF(2007)-004	All LF001 are from an individual ped. LF004 is a resample from 2007
Laguna Guzman	LG003, LG002, LG(07)001, LG(07)004a, LG(07)004b	LG002 and LG(07)001 are from a transitional zone between Laguna Guzman and Fresnal. 003 and 002 are from 2006
Laguna Sta. Maria	LSM(07)002, LSM(07)003	Both samples from 2007
Laguna Palomas	LPAL(07)005	Sample from 2007
Laguna Ascension	ASC(07)001, ASC(07)002, ASC(07)003	All samples from 2007, ASC002 is an efflorescent salt crust

For most sample sites, samples were collected in the form of surface desiccation polygons (peds), except where noted in the sample in which case sample may be specifically from bottom, top or the ultra fine sediment curled crust (flakes) atop the ped. Enough sample was collected in a plastic sample bag by removing the polygon from the surface and manipulating the form as little as possible in order to avoid structural damage, thus facilitating subsampling of the ped. Loose surface flakes were collected using a plastic spatula or dragging the sample using the ped.

Elemental analysis was done by PIXE. Samples were pulverized in a corundum mortar and pestle. An average of 3-5 grams of material was powdered for each sample. An aliquot of approximately 1 gram of each powdered sample was pelletized into a 2.5 cm disk between two Kapton films.

PIXE analysis was performed by a General Ionex 4 MV tandem accelerator with a duoplasmatron source capable of producing beam currents in the range of a few nA to tens of µA, a dual quadrapole focusing lens, an x-y beam scanner to insure beam homogeneity, a beam pulser with 50 ns response time and a vacuum/helium chamber with internal dimensions of 20"w x 16"l x 8"h. The data acquisition system included a computer driving a CAMAC crate front ended with a 150 eV resolution, 30 mm^2 Si(Li) detector for X-ray collection and Au surface barrier detector to monitor scattered protons. Samples were irradiated using a 1.6 cm diameter collimator to enhance overall response for elements and to reduce potential for homogeneity issues. Each pellet was subjected to irradiation such that it was subjected to a minimum number of proton counts (typically 10^6 per sample).

Data reduction was accomplished with the use of software developed at the University of Guelph (2). The efficacy of the analyses was verified using USA National Institute of Standards and Technology Standard Reference Material 2711, Montana II Soil, which was pelletized and analyzed under the same conditions during the same run.

Elemental data were analyzed via descriptive statistics (Mean elemental concentrations shown in tables 2 and 3), correlation coefficients, and analysis of clusters, plotting dendrograms to establish the affinity both among elements and playas in order to attempt to propose feasible geochemical sources (Figure 1). Elemental concentrations were plotted for each playa and its individual samples. A crustal enrichment factor (EFc) was also calculated in order to establish the nature of the elemental concentration and the possibility of anthropogenic contamination of some of the sites. The EFc was referenced to aluminum using Equation 1 and crustal reference values of Mason (3).

$$EFc = \frac{(Cx / CAl)sample}{(Cx / CAl)crust} \quad (1)$$

EFc is the crustal enrichment factor referenced to aluminum. Cx is the concentration of an individual element in the sample, and the crust. CAl is the concentration of aluminum in the sample and the crust.

TABLE 2. Mean Elemental Concentrations by Playa Subsections, Major Elements (percent)
(± range between maximum and minimum, 0 indicates only one sample) (BDM = Bolson de los Muertos)

Playas	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
GV	0.40±.03	1.50±.08	7.01±.16	23.70±1.14	2.54±.13	8.12±.71	0.38±.02	0.06±.003	2.83±.04
CLP	3.63±1.05	1.78±.76	6.40±.23	25±3.25	2.31±.19	7.71±1.17	0.32±.02	0.06±.007	2.60±.53
SELP	3.42±3.99	1.61±.36	5.92±1	24.93±6.45	2.46±.68	8.07±5.8	0.31±.04	0.05±.02	2.35±.78
HWY2	1.54±0	1.26±0	9.04±0	30.20±0	2.83±0	2.17±0	0.46±0	0.10±0	3.68±0
COR	2.99±.24	2.28±.22	6.99±.24	25.32±1.32	2.36±.04	4.28±.87	0.34±.03	0.07±.008	3.73±.15
Total BDM	2.40	1.69	7.07	25.83	2.50	6.07	0.36	0.07	3.04
LF	0.82±.48	1.22±.74	6.17±2.56	19.53±7.53	2.16±.76	3.84±1.90	0.37±.16	0.08±.02	3.77±1.02
LG	1.22±.12	2.02±.22	6.99±.69	24.05±4.51	2.45±.66	6.82±2.09	0.38±.09	0.07±.002	3.26±.21
TLG	1.36±.44	1.72±.59	7.02±.95	24.18±4.21	2.59±.78	8.07±.86	0.39±.009	0.06±.008	3.20±.13
LSM	2.27±1.83	1.50±.15	7.41±.001	26.33±1.60	2.39±.24	3.93±.51	0.53±.02	0.07±.01	3.83±.42
LPAL	0.76±0	1.70±0	7.71±0	24.26±0	1.94±0	4.58±0	0.58±0	0.08±0	3.99±0
ASC	13.51±31.91	0.92±.62	3.92±6.36	15.45±21.3	1.56±2.25	6.18±14.17	0.23±.35	0.04±.06	1.69±2.85

TABLE 3. Mean Elemental Concentrations by Playa Subsections, Minor and Trace Elements (ppm)
(-- below detection limit) (± range between maximum and minimum, 0 indicates only one sample) (BDM = Bolson de los Muertos)

Playas	S	Cl	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Zr	Pb
GV	366±52	--	22±7	22±9	86±6	14±2	--	--	125±38	334±3	208±24	29±0
CLP	2160±1080	14055±20610	13±0	18±0	69±15	12±4	--	32±0	110±2	692±138	152±74	43±10
SELP	5353±9140	30953±65750	--	20±0	71±40	15±0	--	25±16	130±26	702±494	227±152	38±0
HWY2	--	--	--	16±0	94±0	20±0	--	--	129±0	364±0	267±0	--
COR	--	1223±1714	--	--	95±4	--	--	--	--	527±10	--	--
Tot BDM	2626	15410	17	19	83	15	--	28	123	524	214	37
LF	360±353	661±1288	21±11	17±14	115±32	19±9	18±8	--	132±47	420±186	289±130	--
LG	471±206	--	14±1	17±8	87±8	16±6	12±0	--	123±44	629±77	230±7	--
TLG	244±487	749±983	17±1	22±2	106±10	--	18±0	--	143±0	742±133	186±18	55±0
LSM	1664±2533	2347±3686	--	18±6	107±19	20±11	23±0	--	156±8	415±28	327±23	39±0
LPAL	--	--	52±0	27±0	88±0	12±0	17±0	--	97±0	386±0	275±0	--
ASC	13466±33852	105130±1594 40	13±0	8±11	52±88	17±0	132± 171	442±4 98	143±45	523±977	199±280	--

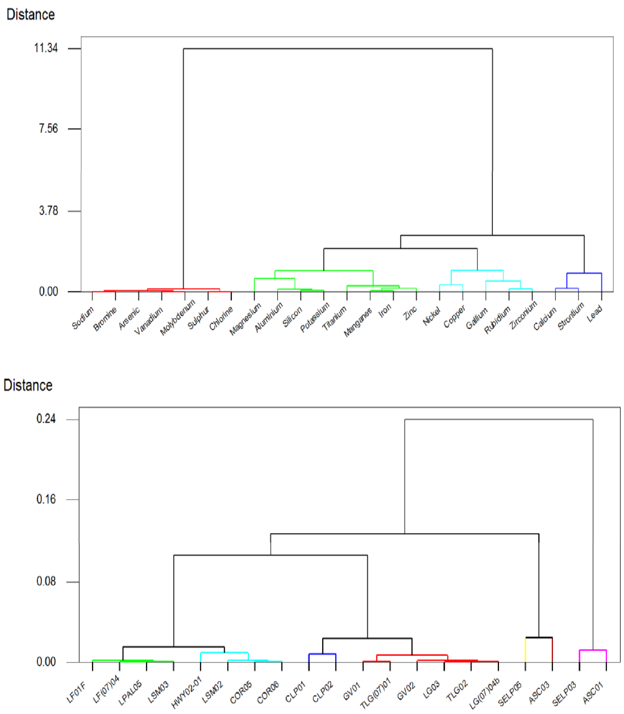

Figure 1. Dendrograms of the elemental concentrations found throughout Pluvial Lake Palomas (top) and dendrogram of the different playa sub-samples (bottom), only two samples per playa were plotted.

RESULTS AND DISCUSSION

Mean elemental concentrations found for the individual basins (playas) are summarized in Tables 2 and 3. The tables are separated into major, minor and trace elements. 23 elements were detected. V and Mo are not included in the tables because they each were only present at one location Laguna Ascension (ASC 002). The ASC 002 V value is 94.7±4.4 ppm while the Mo value is 54.3±8.3 ppm. This sample is composed of an efflorescent salt crust that forms in the sediments of the wet playa shorelines. It is noted that these types of crusts are the first to form when the soils begin to desiccate, and are also the first to erode and disperse into the atmosphere as dust with wind action.

The major element concentrations are mainly distributed below the 10 percent for most elements with the exception of Na and Si. Na exceeds this limit with an outlier at the ASC 001 sample. Si presents the greatest values with a mean above 25 percent for the entire sample suite, and a maximum value over 30 percent. Despite these elevated concentrations all values fall with in the crustal averages as calculated from the crustal EFc. Mn and Ti present the lowest concentration of major elements. Most minor and trace elements in the samples display concentrations well below 300 ppm, with the exception of Br in ASC 002 sample with values close to 690±7.5 ppm. S and Cl have the highest concentrations among the minor elements in the samples, with concentrations that reach 18.4±.2 percent for Cl in ASC 002. Some elements considered hazardous are present in these playas. Elements such as Pb and As are consistently found throughout. Other elements such as V and Mo are only found in one sample (ASC 002) previously mentioned.

Throughput the playas the most common enriched element is Cl. Some of these high Cl scores might be associated with the presence of salts in the playa sediments. The efflorescent sample of ASC 002 is the greatest enriched sample for Cl, S, As, Na, Br and Mo. Na reaches a EFc close to 140, Cl 10,913, S 777, As 1287, Mo 641 and Br 2718. These values are well beyond any crustal average. As observed in a satellite image for the area the site is connected through a drainage system to major agricultural fields. Thus the accumulation of these elements might be related to the industrial products used in these fields.

The samples from Laguna El Fresnal (LF) closely resemble each other with the exception of Cl in the sample collected after the wet season (LF 004). Arsenic is present in all four samples and its values are slightly over 10 EFc leaving room for its origin interpretation. The Bismarck mine, one of the main mineral extraction sites in the area for Sphalerite (Zn and S ore) and Chalcopyrite (Cu, Fe sulfide) discharges its groundwater to Laguna El Fresnal. No appreciable high concentration of these elements is found in any of the samples close to the mine.

Laguna Guzman (LG) is only about 15 km north of Laguna El Fresnal. The Laguna Guzman samples are similar in composition to the LF samples with the exception of Cl only present in LF. Among the individual samples, the main difference is the presence of S and As in the samples after the rainy season with some enrichment of As.

Laguna Santa Maria (LSM) is confined between to mountain ranges in the western area of the PLP. Two samples were collected one representing a regular ped sample (LSM 002) and the other a slightly salty crust (LSM 003). Opposite to the behavior of ASC 002 the salty crust sample is not the enriched one. Cl, As and S have larger values in LSM 002 than in LSM 003. Only Cl and As have EFc scores between 10 and 20.

Laguna Palomas (LPAL) is the northernmost playa surface in the Mexican side of LPL. Its composition is similar to the rest with the exception of S and Cl which are depleted in the sample. With the exception of As all other values are very low in EFc scores, As is just close to 10 EFc.

Among the sub-areas of the Bolson de los Muertos (BDM) the geochemical signature is generally similar with few exceptions: for example the SELP samples where SELP 003 exhibits the presence of Cu, Ga and Pb while the other two samples do not. This suite of elements is also only found in the CLP 001 sample leaving the rest depleted in these elements. Cl is enriched in all areas except for the HWY02 sample area (northernmost area). This sample possesses the lowest EFc factors and is depleted in Cl and S common to most samples. The COR samples are depleted in S, Rb and Zr, common elements in CLP and SELP. These two samples (COR) exhibit the most homogeneity between samples of the same area.

The elemental dendrogram (Figure 1) displays associations among different elements, which could be initially related to existing minerals found throughout the area. Associations are observed between Cl and S: Ti, Mn, Fe, and Zn: Na and Br: Al, Si and K: and Ca, Sr, and Pb: all of these are expected geochemical affinities of the different mineral types likely to be found in the basins. The observed clusters of the playa sub-samples dendrogram corroborate (in most cases) the affinity among sub-samples of the same basin, important due to the large spatial extent of the basins and its possible multi-source sediment inputs. In the same manner exposes the similarities among different basins. The future use of XRD analysis will permit to precisely identify the corresponding mineralogy for each of the associations. These results along with multivariate statistical analyses will improve our understanding of the geochemical associations of different elements, sediment types, and sub-basins of the Pluvial Lake Palomas system

CONCLUSIONS

Proton induced X-ray emission analytical method has proven successful to describe the geochemical behavior exhibited by lacustrine sediment samples from the Lake Palomas basin. Statistical analysis conducted with the use of the PIXE data helped describe geochemical variations and associations, both by element and sampling site. Enrichment factors evaluate the possible anthropogenic origin or anomalous enrichments of several elements and sites. At least in one site (ASC) the observed elemental concentration may clearly be related to anthropogenic enrichment.

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