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PIXE Analysis of Obsidians from Teotihuacan

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Abstract. A collection of about 50 archaeological obsidians studied in the framework of the Preciudadela Project (Teotihuacan, Mexico) has been analyzed using PIXE with the external beam line of the AGLAE facility (C2RMF, Paris) and of the Instituto de Física (UNAM, Mexico). To determine the provenance of these obsidian samples, the elemental compositions derived from the PIXE spectra have been compared with data published in the literature on the basis of instrumental neutron activation analysis (INAA). By looking at the concentrations of some key elements (Na, K, Mn, Fe, Zn, Rb, Sr, Zr, Ba), it was possible to unambiguously assign the provenance of most samples. Many of them are originating from two major sources, namely Sierra de Pachuca I, also known as Sierra de las Navajas (Hidalgo State) and Otumba (Mexico state), the main suppliers of obsidian exploited by the Teotihuacans. However, some samples exhibit a compositional fingerprint matching other provenances: Paredón (Puebla State) and Zacualtipan (Hidalgo State). Special emphasis will be put on the data reduction strategy and statistical tools used to derive the provenance.

Keywords: Obsidian, PIXE, Teotihuacan, Archaeometry.

INTRODUCTION

Obsidian is a volcanic glass mainly composed of amorphous silica and other oxides, with average composition [1] SiO_2 (77%), Al_2O_3 (13%), Na_2O (4.5%), K_2O (4.5%) and CaO (0.5%). Obsidian deposits were formed by quick solidification of volcanic lava flows, resulting in an amorphous glass (not crystallized). The quick solidification from a liquid phase (magma) implies a quite uniform chemical composition, which is not always the case for sedimentary or metamorphic rocks. Although the major constituents of obsidians from different origins are rather constant, trace elements vary strongly from source to source. Therefore, the concentrations of trace elements in archaeological obsidians usually permit to relate them to geological sources of obsidian, and in this way allow tracing the paths of possible trade routes and cultural exchange networks. The compositional uniformity of the restricted number of potentially exploitable obsidian deposits, the marked different trace-element composition of these sources, the availability of comprehensive compositional databases of Mexican obsidian sources [2], and the availability of non-destructive methods of trace-element analysis, like particle-induced X-ray emission (PIXE), are fundamental points that explain the success of the provenance studies on Mexican obsidians.

The Teotihuacan archaeological site is located in the Valley of Mexico, at 45 km NE Mexico City. The first occupation started about 200 BC. At this time (AD 600), Teotihuacan was one of the most important cities in Mesoamerica, extending over a surface exceeding 22 km^2 and had a population of ca. 200000 inhabitants. Teotihuacan was abandoned in ca. AD 650, for some reasons (over-population, internal rebellions, cut of trade routes, etc.). Even as a ruin, this great city retained a great importance, and was never lost. Around AD 100, and probably before, Teotihuacan controlled two of the greatest obsidian sources in Mesoamerica: Otumba [3] and Sierra de las Navajas [4]. The control and mining of these sources by the Teotihuacan State, the manufacturing of arms, tools and ornaments in the Teotihuacan workshops and the strategies undertaken for their distribution and trade were fundamental for the development of this great city and the economic and politic control of hundreds of communities over a large geographical region [5]. Luxury artifacts were also produced and exchanged with the elites of foreign regions, with the aim of extending the political control over remote territories.

The Preciudadela Project, carried out at the INAH under the direction of J. Gazzola, in the La Ciudadela complex, has permitted to unearth some of the oldest Teotihuacan constructions. The numerous and diverse artifacts recovered during the excavation work have allowed to suggest some aspects of the behavior of the inhabitants of this site during the period 0-AD 200 [6]. Obsidian was one of the most abundant materials, and the diversification and quality of the recovered artifacts indicates that Teotihuacan, since the most ancient times, had commercial relationships with other groups exploiting other sources. In this study, a collection of 50 obsidian artifacts has been analyzed at two PIXE facilities: AGLAE (France) and IFUNAM (Mexico) to identify their provenance.

FIGURE 1. Obsidian objects from Teotihuacan, Mexico. The scale is in cm. Photographs by Miguel Morales.

METHODS AND MATERIALS

PIXE analyses were carried out in Paris during June 2006, at the AGLAE (Accélérateur Grand Louvre d'Analyse Elémentaire) facility, based upon a 3-MV tandem tandem accelerator (NEC Pelletron 6SDH-2). An external proton beam of 2 MeV with a diameter of about 100 μm was used and the sample was scanned over a 0.5 x 0.5 mm^2 area in order to obtain an average composition. Objects were placed on a 3-D sample holder monitored by a video camera allowing positioning accurately the exact point of impact of the proton beam, visualized as a luminescent point. X-ray spectra were recorded using two Si(Li) detectors oriented 45º relative to the proton beam, the first being dedicated to measure the low-energy X-rays (0.3–10 keV) emitted by low-Z major elements of the obsidian matrix, and the second high energy X-rays (5–40 keV) emitted by trace elements. A 50-μm Al filter was placed in front of the high-energy detector, and the low-energy detector equipped with an ultra-thin window was operated in a helium flow. Spectra were acquired with a fixed dose corresponding to an irradiation with a 5-nA current during about 7 min. Proper quantitative analysis was checked on the DR-N geostandard (Diorite, CRPG Nancy). Some samples were also analyzed with the PIXE facility of the Instituto de Física (UNAM, Mexico D.F.), which is based upon a 3-MV tandem accelerator (NEC Pelletron 9-SDH). A proton beam of 3 MeV with a current of 5-nA was used during 10 minutes. For each sample, two spectra were recorded using a Ge Canberra LEGe for the heavy elements and a Si-PIN Amptek XR-100CR detector for the light elements, placed at 45° with respect to sample normal [7]. Elemental concentrations analysis were obtained by processing PIXE spectra with the GUPIX code [8,9]. Statistical analysis (correlation and multivariate analyses) has been performed using the STATISTICA software [10].

The samples analyzed consist in a collection of 50 fragments or pieces, mainly fragments of prismatic blades. (table 1). The samples were collected from the excavations conducted during the 2002-2004 period, in the Preciudadela project. Some objects are photographed in Fig. 1. Sample were selected according to their visual appearance: color (green, grey and black), light reflection (silvered or golden) and opacity (translucent, semi translucent or opaque). Several translucent green obsidians, likely originating from Sierra de las Navajas, were included to estimate the ability to differentiate the extraction sites from this geological area.

RESULTS AND DISCUSSION

The elements quantified by the PIXE were Na, Mg, Al, Si, P, S, Cl, K and Ca (major elements); Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb (trace elements, K-lines); and Ba, La, Ce, Hf, Pb, Th, U (trace elements, L-lines). These data were compared to compositional data of obsidian from Mexican deposits found in the literature. The most comprehensive compilation published [2], as well as other data [11] have been obtained by INAA (Instrumental Neutron Activation Analysis). Some elements, such as Rare Earth Elements, commonly measured with INAA are not readily provided by PIXE. Contrarily, some elements are better determined by PIXE (like Ti, Y, Ni, Pb) [12]. However, although the range of elements measured by PIXE and INAA differ, it was possible to define a subset of elements measured by both techniques suitable for comparison.

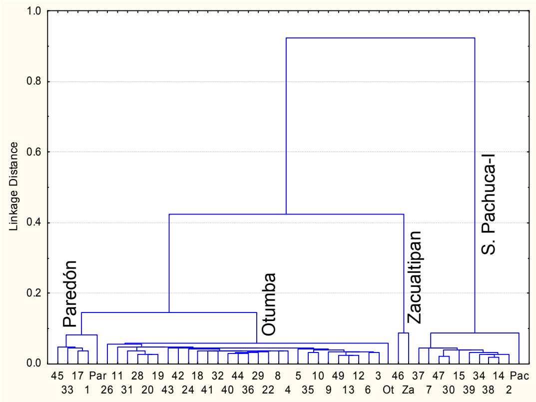

FIGURE 2. Dendogram built using the logarithms of the concentrations of Mn, Fe, Zn, Rb, Zr, for all samples excluding the doubtful ones from a first manual analysis (16,21,23,25,27,48,50) and four references Otumba (Ot in the plot), Zacualtipan (Za), Sierra de Pachuca-I (Pac) and Paredón (Par). It can be appreciated the grouping in four main blocks, each one including a single reference.

Concentrations measured by PIXE agree with those from INAA, as benchmarked in [11]. Therefore, we selected the following set of elements for comparison: Na, K, Mn, Fe, Zn, Rb, Sr, Zr and Ba. The archaeological samples were numbered from 1 to 50 (see Table 1) and the 20 references [2] with negative numbers: -1:Altotonga (Veracruz), -2: Zaragoza (Puebla), -3: Pico de Oribaza (Veracruz), -4: Guadalupe Victoria (Puebla), -5: Derrumbadas (Puebla), -6: Paredon (Puebla), -7: Otumba (Edo. Mexico), -8: Mailpaís (Hidalgo), -9: Tulancingo (Hidalgo), -10: Tepalzingo (Hidalgo), -11: Zacualtipan (Hidalgo), -12: Sierra de Pachuca-I (Hidalgo), -13: Sierra de Pachuca-II (Hidalgo), -14: Sierra de Pachuca-III (Hidalgo), -15: Ucareo (Michoacan), -16: Cruz Negra (Michoacan), -17: Zinapecuaro (Michoacan), -18: El Paraiso (Queretaro), -19: Penjamo-I (Guanajuato), -20: Penjamo-II (Guanajuato). Prior using any statistical tool, we have proceeded to a single-variable manual classification based on the plots of element concentration, versus the sample number. They permitted to assign bands correlating archeological samples with geological references. In particular, a single element (Mn) permitted to clearly assign a collection samples to -12 (Sierra de Pachuca-I). By looking to these plots, in particular to those of Zr, Rb, Sr, it was possible to conclude that most samples come from two sources: 29 from Otumba (-7) and 10 from Sierra de Pachuca-I (-12) (see Table 1), the main suppliers of obsidian exploited by Teotihuacans. However, a non negligible group (samples 1, 17, 33, 45) come from Paredón (-6) and only one (46) from Zacualtipan (-11). This is a remarkable fact, as this source has never been reported in connection with Teotihuacan obsidians [12]. A confirmation of this assignment is obtained by performing a dendogram (Fig. 2), containing these references and the samples that, in principle, do not present doubts in their assignment (all ones excluding 16, 21, 23, 25, 27, 48, 50).

Further discussions and analyses permitted to suggest an assignment for the other samples, keeping in mind, however, that this assignment is not as reliable as the precedent ones. Samples 16, 23, 25 and 27 could be assigned to Otumba (-7), sample 21 and 48 to Paredón (-6), and sample 50 to Sierra de Pachuca I (-12)

A selected subset of samples was measured in the Mexican PIXE facility at the Instituto de Fisica, UNAM. The purpose was to make a cross-comparison of the results, and also study the reproducibility of the results for the same sample. For such a purpose, the same sample was measured up to five times, in different points, and also during different experimental runs (i.e., in three different dates). Two geological references: Otumba and S. Pachuca (S. de las Navajas) were also measured. We observed that, in some cases, the concentration may present a wide variation range (e.g., for M2 we obtained concentrations Ca: 7430 (2435)μg/g, Mn:659(61)μg/g, Rb:133(35)μg/g, with the standard deviation in parenthesis). Attention should be paid to some outliers, for example, the high error in Ca is due that one measurement gave roughly twice concentration that the others. This variability could be due to different reasons. First, the samples are not perfectly flat and smooth, and PIXE is sensitive to these geometrical parameters. The second important reason is the lack of homogeneity of the samples: they are natural samples, and this makes impossible a complete reproducibility. However, this variability does not prevent to classify the samples into provenance groups, as discussed before. In particular, the concentrations of Mn, Zr, Rb, and Sr are good fingerprints for the differentiation. Fig. 3 shows the Zr versus Mn bivariate plot illustrating the excellent separation between Otumba and S. Pachuca-I, but these two variables do not allow to discriminate efficiently between the sources Otumba and Paredon.

A special comment concerns the color and the texture of obsidian. Although most obsidian presents a grey and/or black coloration, green obsidian can be found. The most important source of green obsidian in Mexico is Sierra de las Navajas, in Sierra de Pachuca. In fact, all archaeological samples that we identified to come from S Pachuca present a greenish coloration. Therefore, green obsidian is a good indication of S. Pachuca's provenance. However, it is dangerous to assign provenance from the color, as different colorations may be observed for the same source, while the composition is similar [14].

In summary, we analyzed 50 archaeological samples by PIXE at two facilities, in Paris and Mexico.

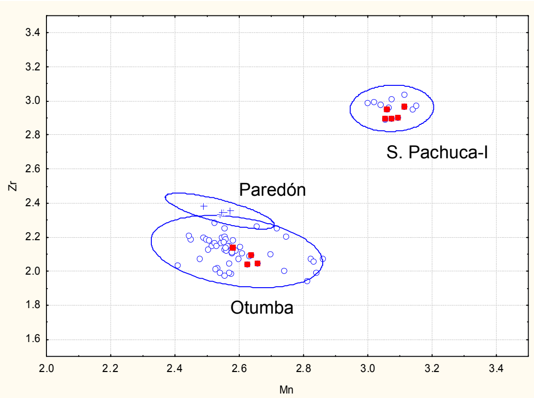

FIGURE 3. Bivariate plot of the logarithm of the concentrations, Zr versus Mn. The Otumba and S. Pachuca-I are well separated. The Otumba and Sierra de Pachuca-I groups contain multiple measurements of 9 samples measured in Mexico plus the values recorded in Paris. For completion, we added the Paris data on the samples belonging to Paredon (+). The measurements on reference samples are marked in black.

Among these samples, 43 could be assigned, without ambiguity, to the two sources well-known to be exploited by the Teotuhuacans, namely Otumba and Sierra de Pachuca, plus two other sources, Paredón and Zacualtipan. The latter was never been reported as obsidian source for Teotihuacans. These results agree with the idea that Otumba and Sierra de Pachuca (Sierra de las Navajas) sources were controlled by the Teotihuacans. They would bring to the city and the Central plateau, raw materials and devices manufactured at the Sierra de las Navajas artisan factories. The higher dispersion of the Sierra de las Navajas' group may also indicate that different sources in this area could have been exploited. (Cobean found three sources S. Pachuca I, II, III, although all samples from S. Pachuca analyzed here belong to S. Pachuca I). Teotihuacans took advantage of the good quality of green obsidian, intensifying its exploitation and expanding its distribution to a number of sites in Mesoamerica with a consequent improvement in their economy. The presence of obsidian from Paredón (Puebla), in the way to Veracruz, might suggest early relationships with other communities in the Central Plateau, and an exchange of resources among these regions in order to fulfill the needs of the increasing Teotihuacan population.

Although some variations were found from different measurements on the same sample, these differences usually do not to prevent a correct assignment. We however recommend to either perform several measurements on different points of the sample, or to scan the beam over a large area of the sample. This study confirms that PIXE is a very efficient technique to determine the provenance of archaeological samples made of Mexican obsidian. In the present case, these analyses confirmed that Teotihuacan maintained trade and cultural relationships with other Mesoamerican regions since the initial phases.

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TABLE 1. List of samples and concentrations in % or μg/g. RSD in all values is 10%. Reference samples (see sites in the text) are marked with negative numbers. Concentrations close to the level of detection (LOD) are marked in italics. Concentrations with values below the LOD are underlined.

Sample	Provenance	Na (%)	K (%)	Mn	Fe (%)	Zn	Rb	Sr	Zr	Ba	Description	Color *
1	-6	2.3	4.4	362	0.9	58	185	*7*	217	*0*	Prismatic Blade	Gray-T
2	-12	3.2	3.9	1230	1.7	230	224	*5*	1030	*0*	Prismatic Blade	Golden Green
3	-7	2.7	3.6	398	0.9	44	138	143	161	935	Prismatic Blade	Dark silver grey
4	-7	2.6	3.6	448	0.9	43	146	143	150	*332*	Prismatic Blade	Opaque grey
5	-7	2.7	3.5	380	0.9	43	147	132	153	*508*	Prismatic Blade	Grey-ST
6	-7	2.7	3.5	404	0.9	44	134	141	151	908	Prismatic Blade	Grey-ST
7	-12	3.3	3.9	1250	1.8	259	234	*5*	1150	*0*	Prismatic Blade	Green- T
8	-7	2.7	3.6	416	1.0	42	148	153	150	*466*	Prismatic Blade	Dark grey - ST
9	-7	2.7	3.6	406	0.9	40	143	124	142	*268*	Flake	Dark grey
10	-7	2.7	3.5	386	0.9	43	129	131	138	*692*	Prismatic Blade	Grey
11	-7	2.7	3.5	382	0.9	38	141	151	158	*0*	Prismatic Blade	Grey-ST
12	-7	2.7	3.5	395	0.9	40	134	134	146	1150	Prismatic Blade	Grey-ST
13	-7	2.7	3.5	401	0.9	41	130	142	151	*410*	Macro flake	Grey-ST
14	-12	3.3	3.9	1180	1.8	236	221	*0*	1100	*242*	Flake	Green-T
15	-12	3.3	3.9	1130	1.7	234	212	*0*	1060	*73*	Prismatic Blade	Golden grey
16	-7?	2.4	3.8	666	0.8	57	154	69	110	*347*	Flake	Red Meca obsidian
17	-6	2.3	4.4	386	0.9	59	194	6	221	*0*	Prismatic Blade	Grey translucent
18	-7	2.6	3.6	459	1.0	43	135	140	152	*651*	Prismatic Blade	Grey-ST
19	-7	2.5	3.6	440	1.1	47	158	161	162	*725*	Prismatic Blade	Silver grey
20	-7	2.3	3.7	461	1.0	47	156	147	160	*652*	Flake	opaque grey
21	-6?	2.2	4.5	299	1.2	43	166	35	243	*211*	ARROW	Black
22	-7	2.6	3.6	432	1.1	47	141	150	163	868	Prismatic Blade	silver grey
23	-7?	1.6	5.3	437	1.0	45	137	155	162	*753*	Prismatic Blade	Grey opaque- ST
24	-7	2.7	3.5	436	1.0	44	126	153	150	*795*	Prismatic Blade	Grey-ST
25	-7?	2.7	3.7	718	0.9	63	171	86	126	*708*	Prismatic Blade	Grey opaque
26	-7	2.9	3.5	422	0.9	41	117	126	142	*408*	BIFACIAL	Grey opaque
27	-7?	1.0	7.7	441	1.0	84	242	167	155	*759*	Prismatic Blade	Grey
28	-7	2.7	3.6	455	1.1	49	159	166	166	*800*	Prismatic Blade	Dark grey
29	-7	2.7	3.6	426	1.0	44	145	142	156	1220	Prismatic Blade	Silver grey
30	-12	3.3	3.9	1210	1.7	227	207	*1*	1000	*30*	Prismatic Blade	Green-T
31	-7	2.6	3.6	475	1.1	49	158	162	179	*719*	Prismatic Blade	Grey/black
32	-7	2.7	3.6	416	1.0	45	141	157	175	625	Prismatic Blade	Grey-ST
33	-6	2.4	4.4	378	1.0	64	196	8	226	*0*	Prismatic Blade	Grey translucent
34	-12	3.0	4.2	1190	1.7	234	230	4	1070	*201*	Prismatic Blade	Golden green
35	-7	2.7	3.5	390	0.9	41	130	148	135	*564*	Prismatic Blade	Grey-ST
36	-7	2.7	3.6	436	1.0	47	137	154	164	*484*	Prismatic Blade	Grey-ST
37	-12	3.3	3.9	1290	1.9	268	250	*4*	1190	*0*	Prismatic Blade	Brown/green-T
38	-12	3.2	3.9	1210	1.8	242	222	*3*	1090	*0*	Prismatic Blade	Green-T
39	-12	3.3	3.9	1230	1.8	238	208	*3*	1080	*0*	Prismatic Blade	Golden green
40	-7	2.6	3.6	437	1.0	45	137	146	160	*848*	Prismatic Blade	Grey-ST
41	-7	2.6	3.6	407	1.0	44	146	155	167	*562*	Prismatic Blade	Silver grey
42	-7	2.6	3.6	470	1.0	44	146	140	163	*461*	Prismatic Blade	dark grey
43	-7	2.7	3.6	389	1.0	48	143	165	163	*505*	Flake	Grey-ST
44	-7	2.6	3.6	424	1.0	46	133	151	172	*354*	Prismatic Blade	Grey-ST
45	-6	2.5	4.4	385	0.9	57	170	*3*	222	*341*	Prismatic Blade	Grey translucent
46	-11	2.2	4.7	177	1.1	36	275	39	218	*243*	BIFACIAL	Black
47 (M68)	-12	3.5	3.8	1180	1.7	222	204	*2*	978	*0*	R. S. Pachuca	Green
48 (M69)	-6?	2.7	4.2	349	0.8	53	158	*3*	176	*0*	??	Grey
49 (M70)	-7	2.8	3.5	389	1.0	42	126	131	155	*366*	KNIFE	Grey
50 (M43b	-12?	1.3	8.5	1350	1.8	265	597	42	1100	*118*	Prismatic Blade	Golden green

*Grey-Translucent: Gray-T, Grey semitranslucent: Gray – ST, Dark grey semitranslucent: Dark grey – ST, Grey opaque+semitranslucent: Grey opaque- ST, Green Translucent: Green-T, Brown/green translucent: Brown/green-T