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The very unusual black backings of two paintings by the Spanish master Murillo (1617-1682) representing Passion Scenes, on display at the Louvre museum, have been analyzed by PIXE with the AGLAE facility of the C2RMF. The support proved to be obsidian, a natural volcanic glass widely employed to produce archeological artefacts, in particular in South and Meso-America. Five archeological artifacts with similar shape to the paintings called "obsidian mirrors", originating from Mexico and belonging to the collections of the *Musée de l'Homme* in Paris, have been analyzed and the composition of four of them showed to be very similar to Murillo's obsidians. The comparison with the results obtained on reference obsidian samples from Mexican sources and with data from the literature by instrumental neutron activation analysis (INAA) suggested that the Ucareo/Zinapécuaro, Michoacán, Mexico is the source of the obsidian employed for the paintings. A field trip to this area was therefore organized to collect samples whose natural slab shape and chemical composition confirmed the Ucareo provenance hypothesis. The rectangular backing of Murillo's paintings are unlikely archaeological artefacts but rather objects specially made after the Spanish conquest by Mesoamerican craftsmen, among which some were exported to Europe where Murillo spent all his life. The observation, in the walls of the church and other Christian monuments in Ucareo, of obsidian inlays, a material of particular significance in the pre-Hispanic culture, underlines the complex intrication of native culture and European influences which are also carried by Murillo's paintings. Meanwhile, a third painting on obsidian by Murillo as been identified in the Museum of Fine Arts of Houston, Texas, U.S.A. This study also points out that even if the ranges of elements dosed by PIXE and INAA do not fully overlap, the measurements obtained by both techniques can be efficiently used for provenancing obsidians objects.

Keywords: PIXE; INAA; obsidian; provenance; paintings; Murillo; Mesoamerica.

Los inusuales soportes negros de dos pinturas representando Escenas de la Pasin del maestro español Murillo (1617–1682), expuestas en el Museo del Louvre, han sido analizadas por PIXE en las instalaciones AGLAE del C2RMF. El soporte mostr ser obsidiana, un vidrio volcánico ampliamente empleado para producir artefactos arqueolgicos, en particular en Sur y Mesoamérica. Se han analizado cinco artefactos arqueolgicos originarios de Mexico, con forma similar a las pinturas llamados "espejos de obsidiana" y pertenecientes a la coleccin del *Museé de l'homme* en París, se encontró que la composicin de cuatro de ellos es muy similar a las obsidianas de Murillo. La comparacin con los resultados obtenidos en muestras referencia de obsidianas de fuentes mexicanas y con datos de la literatura por activacin neutrnica instrumental (INAA) sugiere que la fuente de las obsidianas empleadas para la pintura es Ucareo/ Zinapécuaro, Michoacan, en Mexico. Por lo tanto, se organiz un viaje de estudios a ésta área para colectar muestras cuya forma natural en bloque y composicin química confirmaran la hiptesis de la procedencia de Ucareo. Los soportes rectangulares de las pinturas de Murillo son improbablemente artefactos arqueolgicos, son más bien objetos especialmente hechos por los artesanos mesoamericanos después de la conquista española, algunos de ellos fueron exportados a Europa, donde Murillo pas toda su vida. La observacin en las paredes de las iglesias y otros monumentos cristianos en Ucareo de incrustaciones de obsidiana, un material de importancia particular en la cultura prehispánica, subraya la compleja intrincación de la cultura natal y las influencias europeas que también son llevadas por las pinturas de Murillo. Mientras tanto, en el Museo de las Bellas Artes de Houston, Texas, U.S.A. ha sido identificada una tercera pintura sobre obsidiana de Murillo. Este estudio también indica que incluso si el rango de elementos cuantificados por PIXE e INAA no se superpone completamente, las medidas obtenidas por ambas técnicas pueden ser usadas eficientemente para determinar la procedencia de objetos de obsidiana.

Descriptores: PIXE; INAA; obsidiana; procedencia; pinturas; Murillo; Mesoamérica.

PACS: 82.80.Ej; 91.65.Rg; 91.65.Nd

1. Introduction

Two paintings of the Spanish master Bartolomeo Esteban Murillo (1617-1682) entitled *Agony in the garden* (Fig. 1) and *Penitent St Peter kneeling before Christ and the column* exhibited in the Louvre Museum (Paris) have been analysed by PIXE. For these works, the artist has employed a dark mineral support to render the darkness of the background by leaving a considerable area unpainted. The initial issue was to confirm that this support of these paintings is actually obsidian, a natural volcanic glass and not some black marble as supposed since the 17^{th} century [1–3]. The PIXE analytical method was employed because of its non-destructive character and ease of use, especially for such large items. We also compared the composition of these obsidian slabs with that of archaeological obsidian slabs labelled "*smoking mirrors*" from the *Musée de l'Homme* and the *Musée National d'Histoire Naturelle* in Paris. In a second step, we attempted to determine the origin of these artefacts by comparing their composition with that of obsidian samples from various Mexican geological sources obtained by PIXE. Finally, we compared these results with data from the literature obtained by instrumental neutron activation analysis (INAA) on a larger set of obsidian samples from Mexico.

2. Experimental

The PIXE analyses were carried out with the external microbeam of the AGLAE facility of the *Centre de Recherche et de Restauration des Musées de France* [4,5]. This ion beam facility is based upon a 2-MV Van de Graaff tandem electrostatic accelerator from NEC company (Pelletron 6SDH-2). In the external beam line, the 3-MeV proton beam is brought to air through a 0.1-μm thick Si_3N_4 foil, and focused to a diameter of 30 μm on the target surface with a triplet of magnetic quadrupole lenses. Two X-ray detectors were used to determine in a single run the bulk composition and the trace elements of the samples. The first detector, equipped with an ultra-thin window and a flow of helium gas between detector window and the target surface, was used to measure low-Z elements which are the main constituents of obsidian ($10 < Z < 27$). With a 50-μm aluminium filter, the second detector allowed to measure the high-Z elements (Z>26) present at a trace level. The two detectors, oriented 45° relative to the beam axis in the horizontal and vertical planes, have an active area of 10 and 50 mm^2, yielding a solid angle of 0.002 Sr and 0.260 Sr, respectively. Each sample was placed on a motorised holder (Fig. 2) and analysed on three spots. To average possible compositional heterogeneities probed by the 30-μm diameter beam, the sample were mechanically rastered so the beam covered a square area of 0.2×0.2 mm^2. The beam intensity was 0.4 nA and the integrated charge 0.2 μC. Quantitative analyses were obtained by processing the two spectra recorded on each spot (Fig. 3) with the GUPIX program [6]. The procedure employed allowed to quantify major and trace elements without the need to measure the integrated charge, which is notably unreliable in air. The major constituents were obtained from the first spectrum by scaling the sum of the concentrations in oxide to 100%. The iron concentration computed in this first step was subsequently used as an internal standard in the processing of the second spectrum, normalising the trace element concentration to a correct value. This procedure, which has the advantage to be insensitive to count loss and detector geometry, was checked against a pellet of reference geochemical standard (Diorite DR-N). In addition, the composition of one of the obsidian samples by PIXE has been compared with data obtained on the same sample by ICP-MS. As can be seen in line 1 and line 2 of Table I, the trace element concentrations

FIGURE 1. *Agony in the garden* (ML 931), one of the two paintings investigated made by Murillo on an obsidian slab. Photo J.-P. Vandenbossche, C2RMF.

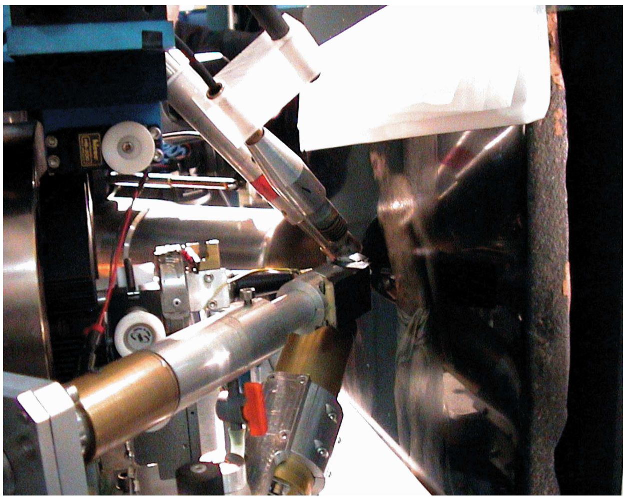

FIGURE 2. View of the second painting, *St Peter kneeling before Christ* (ML 932), positioned in front of the external beam set-up of the AGLAE accelerator. Photo J.-C. Jamet.

TABLE I. Elemental composition of obsidian objects and reference samples. Major elements are given in oxide % and are formatted with a decimal point. Trace element concentration are given in μg/g and appear without decimal point. MDL stands for the mean detection limit.

Museum pieces	Na_2O	MgO	Al_2O_3	SiO_2	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ce	Hf	Pb	Th
24.13.3403	4.0	0.23	13.1	76.4	0.07	4.6	0.49	0.077	0.021	1.07	5	35	19	155	15	16	120	12	83	8	25	13
24.13.3403 by ICP/MS													18	160	13	22	120	6	74	3.6	31	10
24.13.3404	3.9	0.22	13.0	76.4	0.07	4.6	0.50	0.079	0.021	1.12	7	41	20	145	14	28	120	17	91	10	26	18
48.72.2	4.0	0.20	13.0	76.5	0.07	4.6	0.49	0.071	0.020	1.10	7	36	19	145	14	22	130	18	88	4	23	25
78.1.498	5.6	0.24	11.7	75.8	0.14	3.5	0.15	0.190	0.166	2.45	6	220	38	140	1	120	1090	115	91	31	30	44
176.101	3.8	0.26	13.3	76.7	0.09	4.1	0.73	0.132	0.040	0.79	7	38	17	120	103	9	80	12	220	8	35	21
87.101.568	3.4	0.18	13.0	76.8	0.07	4.7	0.49	0.080	0.022	1.09	4	40	20	130	15	21	115	13	88	9	24	18
Murillo ML 931	3.6	0.17	13.0	76.9	0.06	4.6	0.47	0.074	0.018	1.05	3	34	19	130	11	23	110	16	87	8	48	23
Murillo ML 932	3.5	0.18	13.1	76.9	0.05	4.7	0.48	0.079	0.019	1.07	3	38	18	130	13	22	110	14	120	10	45	15
Geological samples																						
Pachuca, Hidalgo	5.7	0.17	11.8	75.3	0.18	4.1	0.12	0.179	0.146	2.34	1	230	37	190	2	130	1120	121	150	29	26	40
Zinapécuaro Michoacán	3.6	0.21	13.2	76.8	0.05	4.5	0.50	0.070	0.021	1.05	8	43	21	130	12	19	110	15	93	9	17	25
Ucareo, Michoacán	3.9	0.18	13.1	76.9	0.05	4.5	0.46	0.069	0.021	0.96	7	39	18	120	10	19	100	12	96	6	17	20
Otumba, Edo Mexico	3.7	0.38	14.1	75.6	0.07	3.9	0.98	0.167	0.048	1.20	25	44	20	120	129	18	130	18	180	3	24	23
MDL	0.1	0.05	0.04	0.04	0.02	0.02	0.02	0.010	0.010	0.01	2	1	1	3	2	8	4	3	100	6	6	10

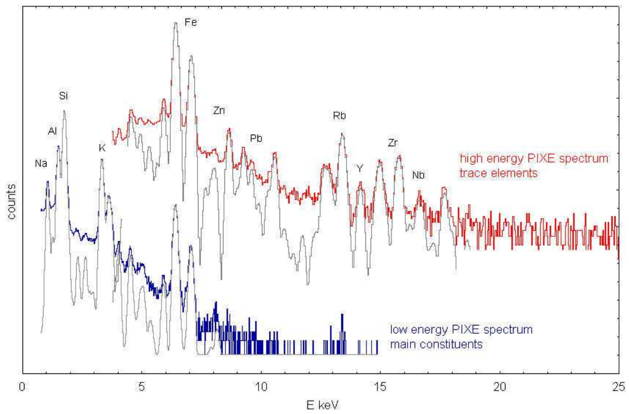

FIGURE 3. PIXE spectra recorded on *Penitent St Peter kneeling before Christ at the column* (ML 932). The bottom curve represents the low-energy spectrum used to determine the major constituents. The upper curve is the high energy spectrum for dosing trace elements. Each spectrum is shown with the fitted line (in grey).

measured by ICP-MS and PIXE in sample ref. 24.13.3403 agree satisfactorily.

3. Results and discussion

The elements measured by PIXE were the following: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb and Ba. From the MDL line (mean detection limit) of Table I, we see that even with very low beam intensity and short measuring time, the sensitivities attained enable the production of useful data for obsidian sourcing studies.

3.1. Comparison with smoking mirrors from museums

The obsidians of the two Murillo paintings were compared to the obsidians of six unpainted archaeological artefacts from Mesoamerica. These objects are called *smoking mirrors* from the translation of the Aztec god name *Tezcatlipoca* which is often represented with a circular mirror made of this material. Except for sample ref. 176.101, the artefacts studied have rectangular shapes and sizes roughly similar to the Murillo slabs (Table II). Other *smoking mirrors* are exhibited in ethnographic or art museums, as in the *Museo Nacional de Antropologia* in Mexico or in the *Museum für Völkerkunde* in Vienna. Although they are generally considered to come from Mesoamerica, it is still unclear whether the less frequent rectangular-shaped mirrors are pre-Hispanic or not. The smoking mirrors considered were acquired by museums in Paris at various dates between 1742 and 1948. The compositions of the artefacts are given in Table I. Murillo's obsidians are characterised by low trace element concentrations (expressed in ppm or μg/g): manganese 143 ppm, strontium 12 ppm, rubidium 128 ppm and zirconium 113 ppm. We observe that the two Murillo-painted obsidians and the mirror MH. 87.101.568 from the *Musée de l'Homme* have an almost identical composition, and mirrors MH.48.72.2, MH.24.13.3403 and MH.24.13.3404 (with a slightly higher Na content) are very similar. We also note the striking similar dimensions of Murillo's paintings and mirror ref. MH. 87.101.568. On the contrary, mirror MH.78.1.498 from the same museum presents a markedly different composition, with in particular larger Na, Ti, Fe, Zn, Ga, Y, Zr, Nb, Hf and Th and smaller Al, K, Ca, Sr contents. The round-shaped and most ancient *smoking mirror* ref. 176.101 from the *Mineralogical gallery of the Museum National d'Histoire Naturelle*

TABLE II. Features of the various artefacts analysed :the two Murillo's paintings and six archaeological *smoking mirrors*. Murillo paintings: **Agony in the garden*, ***Penitent St Peter kneeling before Christ at the column.* The date column indicates when they entered the museum collections.

reference	museum (Paris)	shape	dimensions, mm	date
M.L.931*	*Musée du Louvre*	rectangular	$357 \times 263 \times 25$	1785
M.L.932**	*Musée du Louvre*	"	$337 \times 307 \times 23$	1785
MH.78.1.498	*Musée de l'Homme*	"	$210 \times 164 \times 55$	1878
MH.87.101.58	*Musée de l'Homme*	"	$242 \times 226 \times 28$	1887
MH.24.13.3403	*Musée de l'Homme*	"	$262 \times 260 \times 28$	1922
MH.24.13.3404	*Musée de l'Homme*	"	$324 \times 206 \times 38$	1922
MH.48.72.2	*Musée de l'Homme*	"	$390 \times 220 \times 34$	1948
176.101	*Musée Nat. Hist. Naturelle*	lens-shaped	diameter 252×20	< 1742 ?

also markedly differs both from the "Murillo group" and from the preceding artefact by its high Ca and low Fe, Ce and Y contents.

3.2. Comparison with reference samples

For comparision, we have analysed reference samples collected in five Mexican sources: Pachuca (Hidalgo), Zinapecuaro (Michoacán), Ucareo (Michoacán) and Otumba (Edo. Mexico). First, our measurements agree with the results published in previous studies, mostly performed by INAA. The obsidians from the important source of Sierra de Pachuca show a markedly different composition than Murillo's obsidians with a much higher trace element contents (for instance, zirconium 1120 ppm , zinc 220 ppm Zn, niobium 130 ppm). The Otumba source has an overall similar composition but exhibits much higher strontium ($\sim$ 130 ppm) and manganese ($\sim$ 400 ppm) concentrations. Among the different reference sources analysed in this work, only two show a composition comparable with the artefacts: Zinapécuaro and Ucareo. We also note a striking similarity between mirror MH.78.1.498 and the obsidian of the Sierra de Pachuca.

3.3. Comparison with data from the literature

We should point out that most of the works on obsidian sourcing published in the literature were based on measurement obtained by instrumental neutron activation analysis (INAA) and that the lists of elements dosed by the two techniques only partially overlap. For instance PIXE is unable to measure rare earth elements (REE), commonly measured by INAA, because the overlapping of L-lines of these elements with the K-lines of major elements like iron hampers their detection (MDL=100 ppm). The sensitivity of PIXE is therefore too low to measure hafnium (MDL=6 ppm), baryum, lanthanum, cerium (100 ppm), thorium (10 ppm) and uranium (20 ppm) which all are interesting elements to fingerprint obsidians. On the other hand some elements can be measured with a better sensitivity by PIXE than by NAA: titanium (50 ppm), gallium (1 ppm), strontium (2 ppm), yttrium (8 ppm), niobium (2 ppm) and lead (6 ppm). Surprisingly some major elements like silicon or calcium are not readily measured by INAA. Among the twelve elements that are measured by both PIXE and INAA, manganese, iron, strontium, rubidium, zirconium and zinc are the most useful tracers for sourcing obsidians. Moreover, as shown in a previous inter-comparison work applied to the case of Sierra de Pachuca [7], a good agreement has been observed for data obtained by PIXE, ICP-MS and other analytical approaches like INAA.

From a comparison with our own PIXE data on West Mediterranean obsidian sources [8] and with data from the literature on other Mediterranean and peri-Mediterranean sources, one can eliminate a regional origin for this material. In particular, we can exclude the West Mediterranean obsidian source-island of Lipari, which was under Spanish sovereignty in Murillo's time. We have compared our results with data published by Cobean [9], Cobean *et al.*[10], Jimenez-Reyes *et al.* [11] on obsidian from Mesoamerica. The first reference gives the statistics of elemental composition for 20 Mexican obsidian sources: Altotonga, Pico de Oribaza (Veracruz), Derrumbadas, Paredon, Guadalupe Victoria, Zaragoza (Puebla), Malpaís, Otumba (Edo. Mexico), Tulancingo, Tepalzingo, Zacualtipan, Sierra de Pachuca (Hidalgo), Ucareo, Cruz Negra, Zinapécuaro (Michoacán), El Paraiso (Querétaro) and Penjamo (Guanajuato). In addition, we have used the data published in reference [10] for four other sources in Mexico: Magdalena, Tequila, Teuchitlán (Jalisco), Fuentezuelas (Querétaro). Eventually, the results for two complementary Mexican sources were taken from reference [11]: Oyameles (Puebla) and Zináparo (Michoacán). The same paper also gives data for eight obsidian sources from Guatemala. As pointed out by Cobean, manganese is one of the most interesting elements for fingerprinting obsidian. This element is strongly varying from source to source and presents a good homogeneity within a deposit (standard deviation better than 3%). Among the Mexican sources considered, only four have a manganese content below 200 ppm which is similar to Murillo's obsidians:

Zacualtipan, Fuentezuelas, Ucareo and Zinapécuaro. The other sources have a higher manganese concentration: sixteen sources between 200 and 500 ppm (Altotonga, Zaragoza, Derrumbadas, Paredon, Otumba, Tulancingo, Tepalzingo, Malpaís, Cruz Negra, El Paraiso, Penjamo, Zináparo, Oyameles, Magdalena, Tequila, Teuchitlán), and three above 500 ppm (Pico de Oribaza, Guadalupe Victoria, Sierra de Pachuca). None of the considered sources from Guatemala have a manganese concentration below 400 ppm. We have further discriminated between the four Mexican sources having a manganese concentration below 200 ppm using additional trace elements. For instance, the zirconium concentration of Fuentezuelas (620 ppm) was much higher than the average value for Murillo's obsidians (110 ppm) and the rubidium concentration excluded the Zacualtipan source (290 ppm instead of 130 ppm). Finally, as shown in the Mn/Na diagram in Fig. 4 comparing the present results with those given by Cobean, the only two possible sources left are Ucareo and Zinapécuaro, which are distant by 20 kms. It was not possible to discriminate between them, even if it seems that they have a slight different iron and zirconium compositions. The data obtained by INAA for the two sources show that baryum concentrations should be different (150 and 33 ppm, respectively) but these levels are unfortunately too low to be measured by PIXE.

4. Conclusion

The two obsidian supports of Murillo's paintings have an almost identical composition to four *smoking mirrors* from French museums and thus have probably a common provenance. The comparison of the PIXE results obtained on the painted slabs with obsidian samples from various quarries in Mexico and with a survey of INAA data published in the literature strongly suggests that the Murillo obsidians were originating from the Ucareo-Zinapécuaro sources in the central Mexico state of Michoacán. This was later confirmed by a field trip to the region of Ucareo/Zinpécuaro. The composition of the samples collected on outcrops appeared almost identical to that of the paintings. Moreover, we observed that at Ucareo the obsidian naturally occurs in the form of large slabs the thickness of which (Fig. 5) is comparable to that of the objects investigated. Finally, we have noticed that obsidian blocks are inlaid in the walls of the church of Ucareo, a fact that might stresses the will to incorporate in Christian religion introduced by the Spanish conquest a material that carry traditional beliefs of the native Mesoamerican peoples [12]. The Ucareo source, considered by archaeologists as the second in importance after the source of Sierra de Pachuca, has been quarried from the Early Formative period (100-900 BC) till the Spanish conquest [13]. Ucareo and Zinapécuaro sources could in principle be distinguished through their baryum concentration, but its level is too low to be determined by PIXE. The baryum concentration coul possibly be determined non-destructively by XRF to solve this issue.

Although they have a Mexican origin, Murillo's obsidians are probably not archaeological objects dating from the pre-Hispanic period. Indeed, the rare obsidian mirrors ex-

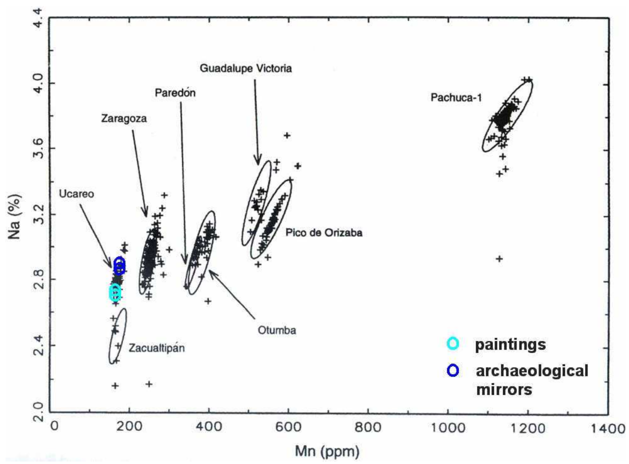

FIGURE 4. Plot of Na concentration (%) vs Mn (μg/g) for the obsidians. The diagram is adapted from Ref. 9. The points corresponding to the two archaeological mirrors and the paintings supports coincide with data from Ucareo obsidian samples.

FIGURE 5. Outcrop of obsidian at Ucareo. Note that obsidian naturally occurs in the form of slabs.

FIGURE 6. *The Nativity*, Museum of fine arts of Houston, Texas, USA.

hibited in museums that have a rectangular shape were never found in an archaeological context which would have allowed one to relate them to a past cultural period. These slabs were more likely artifacts specially manufactured for the Europeans by Mesoamerican craftsmen after the Spanish conquest. If we consider that Murillo has spent most of his life in Seville, whose harbour was receiving freights shipped from the Americas, we can presume that the Master had the opportunity to make use of this unusual dark and brilliant material that brings such a dramatic tension for the representation of Passion Scenes. We should also mention that following the publication of the paintings in the Burlington magazine [2] a third painting of Murillo on obsidian named *The nativity* (Fig. 6) has been identified in the collections of the Museum of fine Arts of Houston, Texas, USA [14]. The analysis of the obsidian of this painting with should shed some light the subject.

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