PIXE in the study of archaeological and historical glass

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Abstract. The PIXE method, especially when carried out with an external beam, is a remarkable tool for the scientific investigation of objects of cultural heritage. We present here two case studies addressing important issues of archaeological and historical glass: de-formulation of ancient glass recipes, determination of provenance of raw materials and understanding weathering processes endangering these precious artefacts. It is also the occasion to specify the place of the PIXE technique among other analytical methods based on radiations for the study of this specific material. In the first example, PIXE was used to determine the provenance of a natural glass, obsidian, constituting the support of two paintings of the Spanish master Murillo (17th c.) on display in the Louvre museum. The comparison of the chemical fingerprints obtained by PIXE with an obsidian composition database established by INAA and XRF showed that the rectangular obsidian panels were imported from Mexico. These investigations also permit to highlight the complementarity of these analytical techniques. In the second example, PIXE was applied to a 12th-century stained glass window from the Saint-Denis basilica (Paris) to determine the various medieval glass (soda- and potash-types) employed in this panel. In addition, by combining p-PIXE with He-PIXE, PIGE, p-RBS and He-RBS, alteration markers of the glass surface, useful in conservation science, were evidenced.

Keywords: PIXE, PIGE, RBS, glass, obsidian, provenance, Murillo, painting, stained glass, weathering.

INTRODUCTION

Glass is widely represented in cultural heritage collections. As a material, glass can be defined as an inorganic melting product that solidified without crystallization. Men has employed obsidian, a natural glass that occurring in volcanic areas since Prehistoric times. Production of artificial glass started in the middle of the 2nd millennium BC., by melting a mixture made of three components: sand (SiO_2), a fluxing agent made either of *natron*, a natural hydrated sodium carbonate (Na_2CO_3) or of plant ashes, together with lime (CaO). The role of these components is twofold: the flux allows to lower the melting temperature to a convenient value and the lime stabilizes the glass to prevent its dissolution in water[1,2]. For the characterization of glass of cultural heritage, PIXE combines good analytical capabilities with a non-destructive character, specially when carried out with external beams. Through cases studies, we show how PIXE has been adapted to address main issues in the study of ancient glass: specification of glass recipes, determination of raw materials provenance and understanding of its alteration.

HISTORICAL GLASS ISSUES

Manufacture technology

Glasses recipes have constantly evolved through time. From the Antiquity to the 8th c., *natron* from quarries was the major source of flux employed in Na- and Ca-rich glass (soda-lime glass). From the early medieval times (8th c.) onwards, a drastic change occurred in the manufacture of glass. Soda-lime glass was made with water-plant ashes (S*alicornia*) and K-rich glasses (potash-lime glass) with forest-plant ashes (fern, beech). During this period, antique glasses were recycled and mixed with medieval glasses. From that time, the use of glass largely spread and glassmaking became a major creative expression, with the development of refined craftsmanship and technological skills, like for instance for medieval stained glass windows.

Provenance of materials

Glass objects have always been considered as precious items and circulated over a long range. The determination of the origin of glass items has a crucial importance in archaeology as it allows to trace back the procurement routes, trade networks between communities and their evolution through time. Sourcing of obsidian glass is among the earliest applications of PIXE in archaeometry[3]. For example, the direct analysis by PIXE of archaeological artifacts made of obsidian has allowed to highlight the exchange networks by native peoples from the Pacific islands[4]. Indeed obsidian incorporates a large number of trace elements which favors the determination of provenance by chemical analysis. For human-made glass, the situation is more complex because glass recycling has always been a common practice.

From the point of view of PIXE analysis, glass is a convenient target: its main constituents are light ones, and the high-Z trace elements are easily detected by masking the low energy X-rays of the matrix with suitable absorbers. Several improvements have been proposed to enhance PIXE sensitivity for glass, such as selective aluminum and vanadium filters suited to various glass types[5]. Sensitivity usually reaches a few μg/g for transition metals, and several hundred of μg/g for the major elements, a feature appropriate to most provenance studies. However for elements with lines above 20 keV like Sn, Sb or Ba the Compton background induced by PIGE on Na, Al or Si limits the sensitivity to a few 100 μg/g. Rare earth elements are also seldom measurable by PIXE, because of the low production yield of their K-line and the overlap of the L-lines with the strong K-lines of Ca, a main constituent of glass.

Comparison with other Analytical Techniques

In terms of sensitivity, PIXE is nowadays outperformed by orders of magnitude by laser-ablation ICP-MS. However, the craters of ca. 100 μm diameter left by this technique on delicate objects might be undesirable. On the other hand, PIXE has an intrinsic mapping capability and can provide an average value over a large area. PIXE also compares favorably with other X-ray-based techniques such as XRF or SEM-EDS or -WDS. In a study comparing the merits of SEM-EDS, SEM-WDS and PIXE for the characterization of glasses[6], similar performances of the latter was demonstrated. XRF is an attractive alternative technique to PIXE, especially with mobile instruments, but Na is not readily achievable. Moreover to dose the wide range of elements that is obtained in one single PIXE run one need to irradiate the sample at various tube voltages. However using our mobile XRF system we were able to measure Ba

down to a few tens of μg/g, an important element for sourcing obsidians. The interoperability of PIXE with ICP-MS and ICP-AES for provenance studies of obsidian has been demonstrated[7]. Finally, let us mention that most obsidian analyses have been carried out by instrumental neutron activation (INAA), a sensitive but time-consuming method which can also measure rare earth elements. In the first application presented here, we demonstrate that the comparison of obsidian data obtained by PIXE and by INAA, on the basis of a subset of elements analyzed by both techniques, is suitable to infer their origin[8].

Weathering

The alteration of glass by the environment or weathering is a major concern in the preventive conservation of cultural heritage. The increasing aggressiveness of the milieu threatens these precious relics of the past. The weathering of glass has been intensively investigated during the last decades, and the overall picture of alteration process is well established[9,10]. The most common process occurs when the surface of glass is put in contact with an acidic solution (humidity, rain). Alkali (Na, K) and to a lesser extend alkaline earths (Ca, Mg) are leached out of the glass, H^+ ions replacing these ions in the glass structure, leading to the formation of an hydrated layer at the surface. This layer may act as a protective coating, but can also retract, leading to fissures through which the solution can reach the healthy glass, allowing the alteration to go further. In addition, leached anions can combine with the SO_2 or CO_2 gases dissolved in the solution and crystallize at the surface in form of gypsum or syngenite. Under the alkali release by the glass, the pH of the solution may eventually be inverted, leading to the total destruction of the glass surface (congruent dissolution). Ancient glass, notably medieval stained glass, has served as model in the study of ageing of glass employed today for the storage of toxic wastes[11,12].

PIXE Characterization of Glass Surface

Various improvements of PIXE have been proposed to investigate the surface of altered medieval glasses[13,14,15]. The comparison of the Si concentrations yielded by PIXE and by PIGE with the 1779 keV γ-line has been used to estimate the surface modification of medieval glasses[16,17] and the same technique has been employed for Na with the 440 keV γ-line[18]. Another approach combining the processing of PIXE spectra in layer mode, a specific capability of the GUPIX program[19] with RBS trough an iterative procedure has also been proposed[20]. A profiling method based solely on PIXE by rotating the sample has also been developed[21]. With a series of ten PIXE

spectra recorded at various impinging angles between 0° to 70°, it was possible to establish concentration profiles of weathered layers and to determine the structure of silver-yellow layer at the surface of stained glass. In this work, we propose to combine 3-MeV protons and 3-MeV He ions to probe the composition at two different depths (fig. 1): close to the surface with He ions (up to 6µm) and deeper with protons (up to 60 µm). PIGE with protons was used to measure Na deeper inside the glass (up to 78 µm), and RBS carried out simultaneously with protons and He ions permitted to profile the first few µm below the surface.
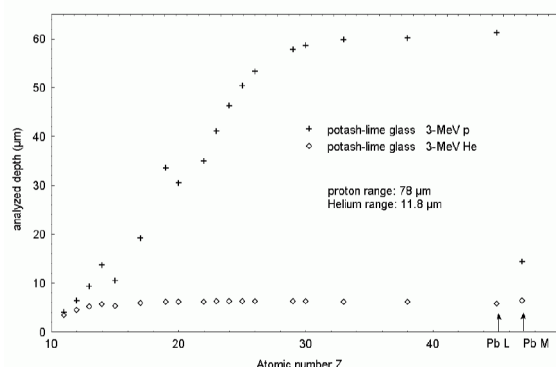

FIGURE 1. Probed depth by PIXE with 3-MeV protons and 3-MeV He ions for various elements in a soda-lime glass. Note the limited value (6 µm) for He ions on elements above silicon.

CASE STUDIES

Two case studies on glass objects from museum collections illustrate the above-mentioned main issues: determination of the origin of the obsidian support of two paintings from the Louvre museum and study of a stained glass window from the basilica of Saint-Denis.

Experimental set-up

The objects were analysed with the external microbeam line of the AGLAE facility[22]. This setup combines four detection channels: two X-ray detectors for PIXE[23], one HPGe detector for PIGE and a surface barrier detector for RBS[24]. The first Si(Li) detector is operated in a helium stream to measure elements from O to Fe (main constituents of the glass), while the second one, with a 50-µm aluminum foil to absorb the strong Si-line emitted by the glass, is used to analyze elements heavier than Ca, mostly trace elements in the present case. The samples were irradiated with 3-MeV protons and helium ions, with an intensity of ca. 5 nA for 5-10 minutes. The beam was focused to a 30-µm diameter on the sample placed 2 mm downstream the 0.1-µm thick exit membrane made of Si_3N_4. No

damage could be observed on the glass. PIXE spectra were processed with the GUPIX package[19] with the assumption that targets were thick and homogeneous and that all elements were in oxide form. Concurrent XRF measurements were carried out with a mobile XRF system developed at the C2RMF, based on a Mo X-ray tube operated at 40 kV combined with a SDD Peltier-cooled detector[25]. Quantitative concentrations were derived from XRF spectra using the WinQXAS program developed at the IAEA[26].

Obsidian Support of Two Paintings by Murillo

The black backings of two works entitled *Agony in the garden* (fig. 2) and *St Peter kneeling before Christ* from the Louvre museum, painted by the Spanish master Murillo (1617-1682), representing Passion Scenes, were found by PIXE to be made of obsidian.

Comparison with Archaeological Smoking Mirrors

The compositions of the obsidian support of the paintings were compared to those of five obsidian archeological artifacts labelled *Smoking mirrors*. The name of these objects is a translation of the name *Tezcatlipoca*, an important divinity in Aztec religion often represented with his right foot replaced with an obsidian disk. Indeed these artifacts that have striking similar shape and size to the paintings originate from Mexico and are conserved in the Musée de l'Homme, Paris.

FIGURE 2. *Agony in the garden* (Louvre ML 931), one of the two paintings made by Murillo on an obsidian slab. © J.-P. Vandenbossche, C2RMF.

Four of them showed an almost identical composition to Murillo's obsidians. These results led us to compare these obsidians of museums with obsidians from Mexican deposits.

Comparison with Obsidian Database by INAA

An extensive compositional database of Mexican obsidians has been established by Cobean and coworkers[27] by INAA. Among the twelve elements measured by both PIXE and INAA for the 26 Mexican sources considered, six elements, namely Mn, Fe, Sr, Rb, Zr and Zn appeared to be most useful tracers for sourcing. As already pointed out in previous studies, Mn is one of the most discriminant elements. The Na/Mn plot of fig. 3 shows that the only Mexican obsidian source that has comparable fingerprint to the museums objects is the Ucareo/Zinapécuaro obsidian deposit, in Michoacán[8].
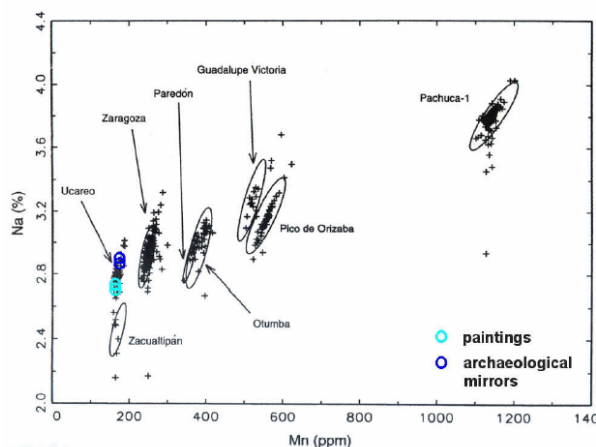

FIGURE 3. Plot of Na vs Mn for the studied obsidians (adapted from[27]). The points corresponding to the archaeological mirrors and to the paintings coincide with those of obsidian samples from Ucareo.

The analysis of obsidian samples collected during a field trip to Zinapecuaro/Ucareo confirmed these results. Surprisingly, we have noted during the trip the presence of obsidian blocks inlaid in the walls of the church of Ucareo. This underlines the syncretism of native Mesoamerican beliefs and Christian influences which, in a certain sense, are also carried by Murillo's paintings[28]. Eventually, this study led to the identification of an additional painting on obsidian by Murillo in the collections of the Museum of Fine Arts of Houston, Texas, U.S.A.

Stained Glass Panel of the Saint-Denis Basilica

We have investigated a stained glass window panel of 50 x 70 cm from the Basilica of Saint-Denis (Paris, France) dated ca. 1140, representing *The Three Wise Men*. Since this glass panel has been removed from the basilica in ca. 1850, it fortunately escaped from the aggressive environment of the industrial era which dramatically altered the other stained glass, that were eventually removed from the building in 1997.

FIGURE 4. Picture of the stained glass panel with the location of the analyzed spots. © D. Vigears C2RMF

The surface of the panel is relatively well preserved, so that these glass pieces are useful for the study of glass recipes of the 12th century and of the weathering of their surface at an early stage. This panel is known for having been restored at various moments in the past (Renaissance to 19th c.) and some non-original parts have already been identified[29]. Fourteen different glasses have been analyzed by simultaneous PIXE, PIGE and RBS with 3-MeV protons and He ions. The location of the analyzed spots is given in fig. 4.

Identification of Original and Restored Parts

From the ternary diagram in fig. 5, we see that most analyzed glasses are either soda-lime glasses (up to 20% Na_2O) or potash-lime glasses (up to 17% K_2O). A close look at the data reveals that five glasses have an irregular composition. The soda-lime glasses BLUE-1, YELLOW-2 and GREEN-3 have no measurable P content (below 200 µg/g), and unusually low Mg concentrations (~0.2% MgO). RED-1 and WHITE-1 are low-soda (2.5 and 6% Na_2O), low-potash (4.7 and 3.6% K_2O) and high-lime (21.5 and 18.3% CaO) glasses. The compositions of these five glasses do not correspond to a medieval recipe[30] and therefore likely correspond to restored parts. BLUE-1, YELLOW-2 and WHITE-2 were already identified in the *Corpus Vitrarum Medii* as restored parts[29], but this information is new for GREEN-3 and RED-1.

Technological and Provenance Markers

The original potash-lime glasses YELLOW-1, YELLOW-3, GREEN-1 and -2, WHITE -2 and -3 and RED-2 and -3 are clearly made of forest hashes. In GREEN-1 and GREEN-2 we found noticeable concentrations of Pb and Sn, that could attributed either to a lead-stannate opacifier or to a lead-tin yellow pigment. In the BLUE-1 restored glass, we found Co (2400 µg/g) in association with Bi (970 µg/g), Ni (1400 µg/g) and As (3200 µg/g). This chemical fingerprint was used to infer the origin of the Co blue pigment employed[30].

Table 1. Cobalt blue pigment grouping according to composition and chronology (adapted from [30])

chemical association	chronological period	ore provenance
Co, Co-Sb, Co-Cu, Co-Mn, Co-Zn-Ni-Fe-Cr-As	from protohistory to 12th c. AD	unknown: local, Near-East
Co-Zn-Pb-In-Fe	13th-15th c. AD	Freiberg Saxony
Co-Ni-Mo-Fe	15th-16th century	Erzgebirge Saxony
Co-As-Ni-Bi-Mo-U-Fe	end 15th – 18th c. AD	Schneeberg Saxony

In table 2, we see that such an association exists for the Co ore mined in the Schneeberg (Saxony) between the 16th and the 18th c. For comparison, the BLUE-3 soda-glass does not contain any detectable amount of Ni, As or Bi associated with Co. The PIXE spectrum of the BLUE-3 glass (fig. 6) show that it contains a high amount of Sb (1.7% Sb_2O_5). The low level of Pb (0.6% PbO) indicates that Sb is not present in the form of lead-antimoniate, a yellow pigment. Sb could have been introduced as an opacifier, but the outstanding transparency of this glass discards this possibility. Sb is more likely used here as a color-correcting agent, in combination with Mn. This blue soda-glass of

exceptional quality, called Near-Eastern or Roman glass, is the only original soda-glass of the panel.
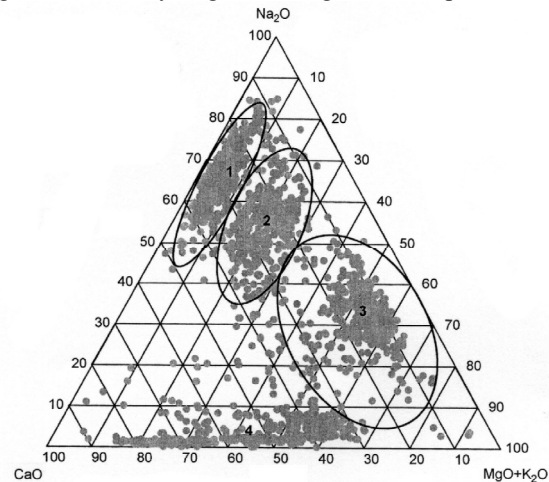

FIGURE 5. Ternary diagrams for the glasses. In the upper diagram, type 1: soda-lime glass with natron, type 2: soda-lime glass with plant ashes, type 3: mixed soda-potash, type 4: medieval potash-lime glass with forest plant ashes (adapted from [30]). Restoration glasses are noted in italic.
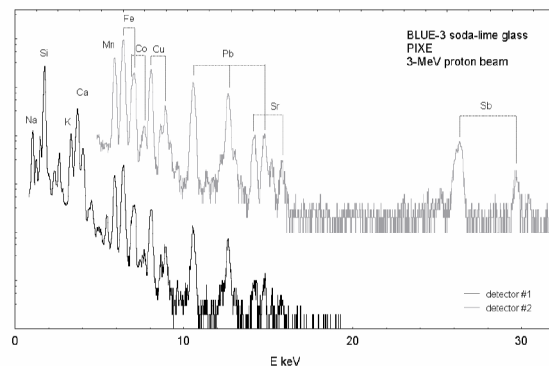

FIGURE 6. p-PIXE spectrum of the BLUE-3 soda-lime glass. Note the high level of Sb.

The aim of this part of the study is to determine the weathering state of two original glasses of the panel: the BLUE-3 soda-glass and the YELLOW-1 potash-glass. To investigate a possible change of composition at the surface, we have compared the PIXE spectra obtained with 3-MeV protons and He ions.

For the BLUE-3 soda-glass, the Na concentration by p-PIXE and He-PIXE were found to be similar (6.7% Na_2O) but the value obtained by p-PIGE threefold higher (19% Na_2O), indicating a strong Na depletion at the surface. This was confirmed by the p-RBS spectrum obtained simultaneously. In fig. 7, a clear displacement of the Na edge towards low energy was observed in combination with a marked increase of O at the surface. This was interpreted by the presence of a 2-μm thick layer of altered glass from which the Na^+ has been leach out and replaced by H^+ ions. This layer was too thick to be measured in the He-RBS spectrum, but on the other hand this spectrum showed an enrichment of Sb at the very surface.
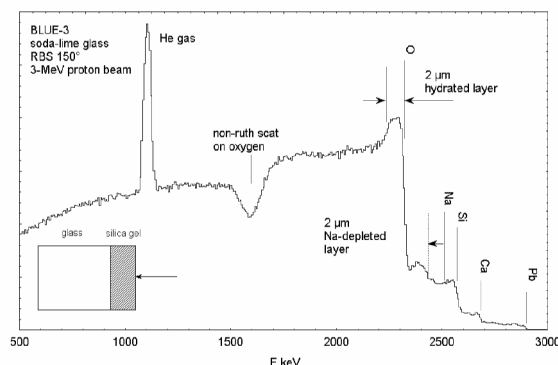

FIGURE 7. p-RBS spectrum of the BLUE-3 soda-lime glass. Note the displacement of Na edge and the O enrichment corresponding to the formation of a 2-μm weathered layer.

For the YELLOW-1 potash-lime glass, the concentration of K by PIXE was found to be a little lower with He ions (14.2% K_2O) than with protons (15.2 % K_2O), suggesting a depletion of K at the surface. This was confirmed by the He-RBS spectrum (fig. 8), where a depletion profile of K over a depth of ca. 2 μm was evidenced. In addition, the He-RBS spectrum showed a sharp peak corresponding to a 10-nm Pb layer at the surface of the glass, topped with a 50 nm glassy layer. This very thin layer might result from the alteration of the lead setting of the window. In the light of the last result, the 2.3 keV peak in the PIXE spectra might be interpreted as the M-line of the Pb thin layer rather than to the presence of S, a common confusion in X-ray analysis.

Because the weathered layers of the two glasses are rather thin (~2 μm), the comparison of PIXE with protons and He ions was not so informative, whilst the information obtained simultaneously by RBS and PIGE was more conclusive. The PIXE combination is better suited to characterize thicker weathering layers which by the way are more common. To sum up, we see that the combination of PIXE, PIGE and RBS provides an accurate view of the weathering state of these glasses, which can hardly be obtained by each analytical technique alone.
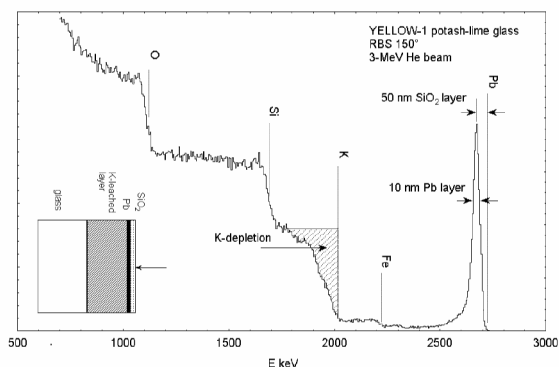

FIGURE 8. He-RBS spectrum of the YELLOW-1 potash-lime glass. Note the K depletion profile and the thin Pb layer corresponding a two-microns leached layer.

PERSPECTIVES

PIXE has been and still is successfully applied to the characterization of archaeological and historical glass, especially with ions beams directly extracted in air. The number and the quality of the published works testify the wealth of this approach. Faced to the emergence of highly sensitive techniques such as LA-ICP-MS or laser-induced breakdown spectrometry (LIBS), PIXE benefits from a total non-destructiveness, an appreciable ease of use, a high rapidity and a good analytical performances thanks to ruggedized analytical setup and procedures combined with reliable processing software. But as was shown in this presentation, the actual strength of PIXE lies in the combination with other techniques carried out simultaneously with the same ion beam, namely PIGE and RBS. The chemical characterization provided by PIXE is now more and more often combined with complementary molecular, structural or dating methods. For instance Raman spectrometry is now used to estimate the polymerisation degree of obsidian[31] and stained glass[32], and when the chemical signature is still ambiguous, other methods such as dating by fission tracks for example, might be helpful[33]. An extensive review of applications of glass from all periods is totally unrealistic, all the more since glass-like materials are widespread in Art and Archaeology, such as enamels[34] or glazes[35] on ceramics. But let us just mention that the combination

of PIXE and RBS was used to evidence the amazing nano-technology developed for the lustre decoration of ceramics[36] and for iridescent Art Nouveau glass[37].

ACKNOWLEDGMENTS

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