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Archeological Applications of XAFS: Prehistorical Paintings and Medieval Glasses

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Abstract

High-resolution manganese and iron K-edges XANES spectra were collected on several samples of archeological interest: prehistorical paintings and medieval glasses. XANES spectra were collected at the ID21 facility (ESRF, Grenoble, France) using a micro-beam device and at the 11-2 beamline (SSRL, Stanford, USA) using a submillimetric beam.

The medieval glasses studied are from gothic glass windows from Normandy (XIVth century). The aim of this study is to help understand the chemical durability of these materials, exposed to weathering since the XIVth century. They are used as analogues of weathered glasses used to dump metallic wastes. These glasses show surficial enrichment in manganese, due to its oxidation from II (glass) to III/IV (surface), which precipitates as amorphous oxy-hydroxides. Similarly, iron is oxidized on the surface and forms ferrihydrite-type aggregates.

The prehistorical paintings are from Lascaux and Ekain (Basque country). We choose in that study the black ones, rich in manganese to search for potential evidences of some “savoir-faire” that the Paleolithic men could have used to realize their paint in rock art, as shown earlier for Fe-bearing pigments. A large number of highly valuable samples, micrometric scaled, were extracted from these frescoes and show large variation in the mineralogical nature of the black pigments used, from an amorphous psilomelane-type to a well-crystallized pyrolusite. Correlation with the crystals morphology helps understanding the know-how of these early artists.

1. Introduction

Recently, a number of XAFS methods have been applied to archeology to help characterize highly valuable artifacts of historical importance such as Medieval gems [1] and Roman glasses [2]. Other applications currently underway include the study of the corrosion of inks used by J. S. Bach (cf. Dahn and co-workers in Berlin, Germany), the corrosion of Celtic weapons (Janssens’s group in Antwerp, Belgium), the determination of growth rate of desert varnish to help dating petroglyphs (Lytle’s group at SSRL) or the sulfur speciation in old and modern woods (see Jalilehvand, this volume).

Archeological studies require some extensive, multi-disciplinary studies, as the number of samples can be high and highly valuable (so undestructive). Also μ -techniques are useful to scan the sample heterogeneities, which can help highly to provide more clues on origins, uses and goals of the artifacts probed. For instance, extensive corrosion studies of Celtic weapons require a thorough study of the pre-edge feature of Fe at its K edge. From the pre-edge feature, accurate mapping of the iron redox can be achieved, which evidence, in the case of these weapons, some very localized areas (microns) of less corroded metal. Such

characteristics can be used as tracers for some past technologies, commercial exchanges, creative actions (composers) or even legends. Surprisingly, we observed that reference studies are missing to help archeologists to perform their characterization in a robust manner. For instance, few studies exist to accurately determine the redox state of Mn from the analysis of its pre-edge feature at the K-edge.

Similarly, manganese shows large variation in redox and speciation, due to the large number of possible redox states that Mn can adopt under ambient conditions (metal, II, III, IV, V, VI and VII). As a result, studies of artifacts in which manganese plays a key role (such as pigments) are essential to trace past technologies. However, extensive studies of the redox of manganese are lacking. They might be useful also for other domains such as geochemistry and material sciences. In this study, we present a XANES study of a large number of Mn-bearing mineral samples in which the pre-edge feature is understood under the light of *ab initio* calculations. The obtained results are applied to the study of black prehistorical paintings (in which manganese dominates) and in medieval glasses (in which manganese is diluted at the 1–2 wt.% level).

2. Experimental

Mn K-edge XANES spectra for model compounds and archeological artifacts (pigments and glasses) were collected under high resolution conditions (~ 0.6 eV) at SSRL (Stanford, USA) using beamline 11-2, Si(220) double-crystal monochromator, 0.3 vertical height for the slits before and after the monochromator. The energy reproducibility of the monochromator is ~ 0.05 eV. Pre-edge features were collected using 0.1 eV steps whereas the main edge crest were collected with 0.3 eV steps to 300 eV above the absorption edge. Self-absorption effects were taken into account as the archeological samples could not be optimally prepared. Then, the XANES spectra were collected in the fluorescence mode. Several model compounds were used to check the accuracy of these corrections (using the code FLUO [3] and transmission data). In parallel, micro-XANES spectra were collected in order to map at the micron scale the manganese speciation. A Si(111) monochromator and a Fresnel focusing device were used at the ID21 beamline at ESRF (Grenoble, France). Spectra were collected in the fluorescence mode using a pin-diode and, when necessary corrected for self-absorption.

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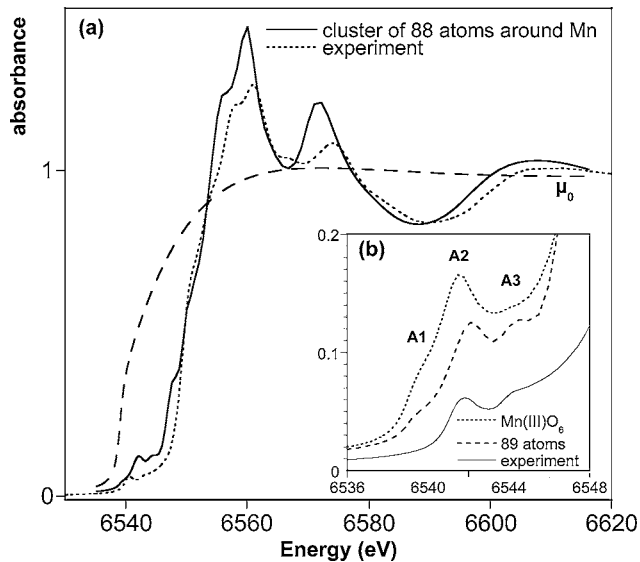


Fig. 1. (a) XANES and (b) pre-edge feature in manganite, (Mn(III)OOH): experimental (solid lines) versus *ab initio* calculations (FEFF, dotted lines), showing the importance of next-nearest manganese neighbors in the pre-edge feature (feature A3).

Mn-bearing model compounds include numerous oxides and silicates, natural or synthetic, well characterized and containing Mn(II,III,IV,V,VI,VII) in octahedral, square planar, cubic or tetrahedral geometry. The archeological artifacts include black pigments from the Lascaux cave (Dordogne, France—18,000 years old) and medieval glasses (more or less weathered) from various gothic buildings (XIVth century BC) from Normandy (France) such as Ste Opportune du Bosc.

3. Results

3.1. Model compounds

Figure 1a shows normalized, self-absorption corrected XANES spectra collected at the manganese K-edge in a typical model compound, namely Mn(III)OOH. Figure 1b shows its normalized pre-edge, obtained using a method described elsewhere [4]. The obtained pre-edge features for a given redox and geometry shows large variation among themselves, suggesting that the Mn-speciation is not the only contributor to the spectra. This is confirmed by *ab initio* calculations of the XANES (including the pre-edge feature assuming dipolar and quadrupolar transitions) performed using the FEFF8.28 package [5]. When the medium-range environment around manganese is included in the model, the pre-edge feature area increases, sometimes up to a factor 2. Multiplet calculations performed by F. de Groot on Mn(II,III,IV)O₆ clusters (*pers. comm.*) also confirm this observation: the calculated pre-edge with multiplets is, especially for Mn(IV), much smaller in area than that measured. A similar phenomenon was already observed for Fe-bearing oxides, for which the pre-edge features show transitions related to next-nearest Fe neighbors [6]. Based on these observations, we could find a strategy to consider only the transitions in the pre-edge feature related to the Mn-speciation (redox and geometry). In order to achieve this, we modelled the pre-edge with pseudo-Voigt lines with a fixed width and Gaussian percentage (1.3 and 45%, respectively). Only the first lines (2 for Mn(II) and Mn(III) and 3 for Mn(IV)) were taken into account (see Fig. 2) to

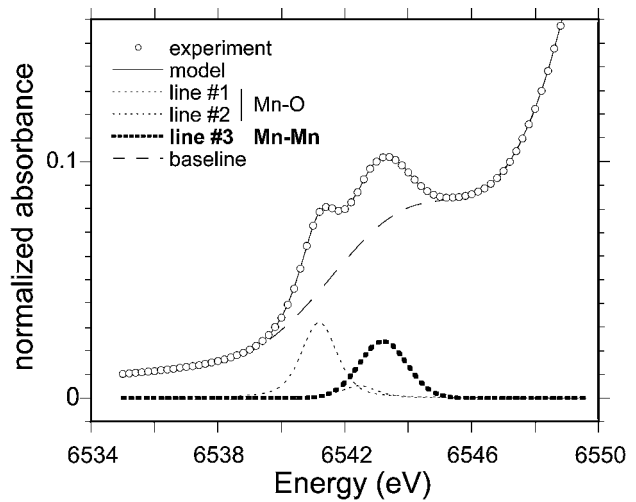


Fig. 2. Example of pre-edge model for Mn(IV), considering lines related to the Mn-O moiety and lines related to more distant Mn neighbors.

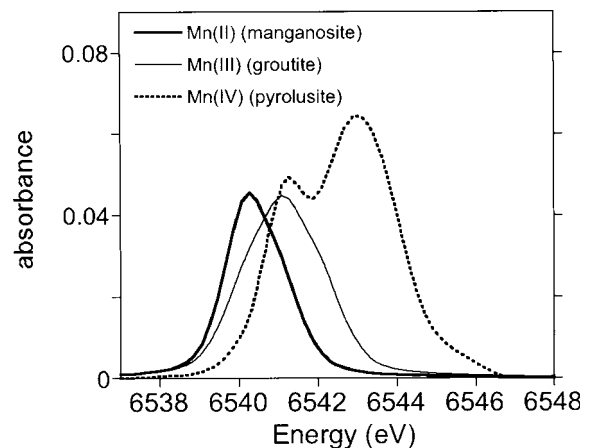


Fig. 3. Shift of the normalized pre-edge feature with Mn-redox, when transitions related to distant Mn are excluded.

derive robust redox and geometric information. As for Fe [4], the pre-edge information must be calculated based on the pre-edge centroid (weighted by the respective area of each line) versus its integrated area. When taken into account, the Mn pre-edge centroid shifts nearly linearly with redox (Fig. 3) and follows *ab initio* predictions.

3.2. Prehistorical paintings

Mn K-edge XANES spectra were normalized following the same protocol as the one for the model compounds. The samples were previously characterized using a wide combination of other methods, such as imaging (TEM and SEM, transmission and scanning electron microscopies, respectively), diffraction (electronic) and chemistry (EDXS and PIXE, energy dispersive and particule induced X-ray spectroscopy/emission, respectively). PIXE information was used to provide chemical information required for self-absorption corrections. For instance, two pigments from the “Great Black Bull” (GLAS65) and the “bichrome horse” (GLAS66) from the Painted Gallery (Fig. 4) show large differences in manganese speciation related to the

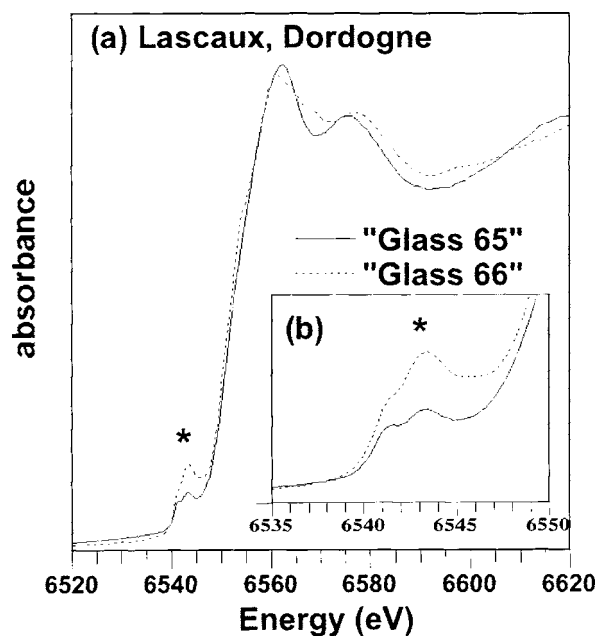


Fig. 4. Mn K-edge XANES spectra for 2 Lascaux pigments from the “Great Black Bull” (GLAS65) and the “bichrome horse” (GLAS66) from the Painted Gallery, showing changes in the XANES (a) and in the pre-edge feature (b) related to the presence of romanechite and pyrolusite.

presence of romanechite and pyrolusite. However, neither the XANES nor the morphological studies performed for these samples evidence the presence of any heating that would have modified the texture of these pigments prior to the painting [7]. 2D mapping experiments of the manganese K-edge XANES were carried out and are still under reduction to determine if some other paintings were manufactured from primary Mn-ore or from heat-treated ores.

3.3. Medieval glasses

Several medieval glasses were examined to study the weathering of the glass windows. Since the XIVth century, these glasses suffered from corrosion, especially the ones exposed to the outside (corrosion from water, pollution, seasonal changes etc.). Some samples were recovered from the building and show a progressive corrosion, as a function of their exposition to weather. Manganese K-edge spectra (Fig. 5) show a progressive shift of the Mn K-edge from the “fresh”, unweathered glass (protected) to the highly corroded areas of the glass. In the fresh glass, manganese is divalent (as in most glasses) and in a “silicate”-type environment. When weathered, manganese oxidizes to +IV and forms environments close to these for manganese oxo-hydroxides (this promotes a surficial enrichment in manganese). A Principal Component Analysis of these spectra reveals that 2 end members can be extracted by inversion. These pure end-members (fully fresh and fully weathered) confirm these trends. This explains why the inside luminosity of medieval building is affected by the precipitation of these complex manganese hydroxides. Similar observations were made at the iron K-edge, where ferrihydrite-type materials precipitated in the corroded zones.

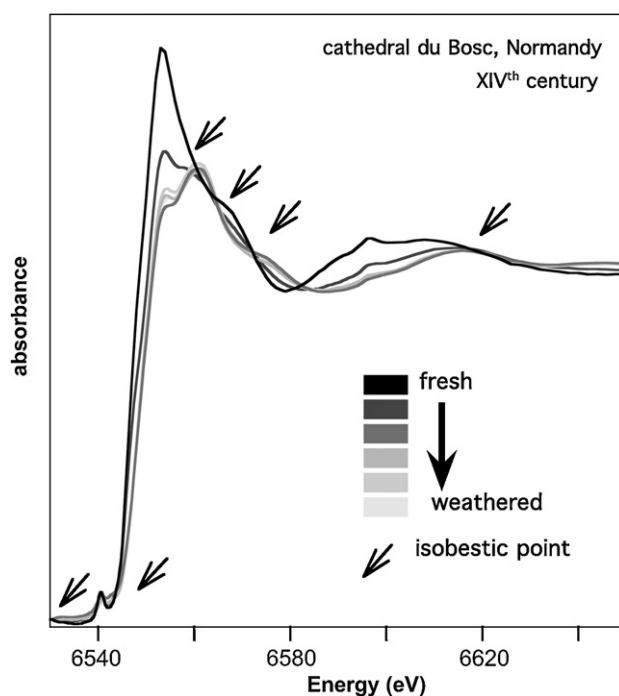


Fig. 5. XANES Profile at the Mn K-edge as a function of the glass thickness for a medieval glass window exposed to progressive weathering (from dark – “fresh” glass to light “weathered”). The data shows an oxidation of manganese from II to IV, which resulted in precipitation of manganese oxo-hydroxides at the origin of the darkening of the building. Isobestic points shows the number of knots in that data set of 6 spectra, suggesting that 2 end members can be extracted by inversion as suggested by PCA analysis.

4. Conclusions

The availability of optimized sources, providing high-resolution, low noise and focusing techniques makes it an unique tool to study highly valuable samples from archaeologists. However, more methods (to diagnose reliably redox and speciation) are needed to help the archaeologists to accurately interpret their data. The main information that synchrotrons can provide is less matter/beam interaction (as compared to proton or electronic sources), drastic improvements in beam source, optics and detection. If “standard” laboratory methods are still required to first investigate these samples, X-ray absorption methods provide important information on redox and environments that can be used to source an origin or a technology. In some other cases (such as for medieval glasses presented here), archeological artefacts provide an interesting outlook on how materials can be preserved or react to ageing. This information is also important for curators to conserve their artefacts or for physicists and chemists to better understand material durability (for nuclear wastes for instance).

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