



Ancient Chinese blue-and-white porcelain glazes: can we measure the oxidation state of cobalt through X-ray absorption spectroscopy?

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Key-words: Cobalt speciation, XANES, blue glazes, Chinese porcelains

Abstract

Archaeological findings of ancient Chinese porcelains can contribute to set up dating processes once the composition of cobalt blue pigments is known to have changed between the 14th and the 17th century. A study of blue-and-white porcelain shards recovered during recent excavations was carried out by non-destructive laboratory X-ray fluorescence spectrometry for chemical characterization, combined with X-ray absorption spectroscopy using synchrotron radiation to ascertain the coordination of pigmenting cobalt ions and infer the corresponding formal valence. A detailed analysis of the near-edge region of Co 1s X-ray absorption spectra (XANES) was carried out on the blue-and-white glazes from those porcelain fragments. Pre-edge features and edge details are discussed in comparison with spectra obtained from model compounds with known crystal structure – Co₃O₄, CoAl₂O₄ and Co₂SiO₄, plus a cobalt-based blue pigment (cerulean, Co_{2-x}SnO₄).

Chemical data allowed to validate the manufacture period of studied Chinese porcelains advanced by Art Historians on the single basis of stylistic features (late 16th and medium 17th cent.) and the spectroscopic results confirm a coordination environment of pigmenting Co²⁺ ions close to tetrahedral, substantiating the dual role of cobalt as network former plus modifier in the glaze of ancient Chinese porcelains. Furthermore, the present study confirms the questionable validity of inferring the oxidation state of 3d transition metal ions wholly from X-ray absorption spectroscopy data.

Introduction

Ancient blue glazes owe its colour mainly to copper and cobalt, either employed separately or added together to the siliceous matrix in order to attain the desired tonality. Once the speciation state of the chromophore elements controls the final colouring effect, a particularly suitable technique to interpret pigmenting performance through non-invasive assays is X-ray absorption spectroscopy (XAFS) using synchrotron radiation. Indeed, the analysis of both near-edge features (XANES) and extended fine structure (EXAFS) has been extensively and

successfully used to study the speciation state of chromophore ions and modifier elements in ancient glassy materials.

The trade of Chinese blue-&-white porcelains to Europe became intense after the maritime contact established by the Portuguese navigators by the end of the 16th century. European museums and traders face nowadays an increased need for establishing the authenticity of such art objects through non-destructive assays. As a contribution, a set of Chinese porcelain fragments recovered during archaeological excavations recently conducted in the Monastery of Santa Clara-a-Velha at Coimbra and in Lisbon Old-city were studied by combining a bulk chemical characterization using X-ray fluorescence spectrometry and XAFS to ascertain cobalt coordination & speciation state(s). Following first approaches [1,2], the theme is developed with emphasis on the questionable formal valence(s) of cobalt ions.

Dating of studied archaeological Chinese porcelain shards

Ancient Chinese porcelains were lately the object of compositional studies applying analytical techniques based on X-rays and neutron beams to find out production periods and sites [3-5]. A set of Chinese shards supposedly manufactured in late 16th to early 17th century was selected for the present study by visual inspection. A shift from imported As-rich Persian cobalt pigments towards Mn-rich native Chinese blue pigmenting ores – asbolane, a cobalt-rich manganese wad with general formulation $(\text{Co}, \text{Ni})_{1-y}(\text{MnO}_2)_{2-x}(\text{OH})_{2-2y+2x}$ – is known to have occurred during the early Ming Dynasty (AD 1368-1644) [6]. Accordingly, arsenic content combined with Fe/Co & Mn/Co ratios configure a suitable dating criterion [7] that supported the manufacture period suggested by Art historians on the basis of a stylistic analysis [1].

Experimental and materials

Co 1s X-ray absorption spectra were collected at the ESRF (Grenoble/France) using the instrumental set-up of beamline BM-29 (recently succeeded by the renewed line BM-23), by applying a Si(111) double-crystal monochromator with detuning for harmonic rejection, thus assuring an energy resolution around 0.8 eV close to the cobalt absorption edge. The surface of glazed debris was directly irradiated to detect the fluorescence yield using a 13-element germanium detector. Pressed pellets of slightly grinded model compounds mixed with boron nitride were prepared in a proportion adequate to optimize the absorption jump while minimizing the total absorption, in this way improving the display of pre-edge details and edge features of spectra collected in transmission mode. The energy calibration was assured by irradiating a cobalt metal foil and assigning the first inflection point to 7709 eV.

To model cobalt coordination plus speciation state various compounds were irradiated: the blue oxide CoAl_2O_4 (with spinel-type structure and Co^{2+} ions in regular tetrahedral coordination); Co_2SiO_4 (with olivine-type structure, Co^{2+} with slightly distorted octahedral coordination); Co_3O_4 , also a spinel where the metal occurs in two formal oxidation states (one Co^{2+} ion in tetrahedral coordination and two Co^{3+} ions in octahedral coordination per formula unit); and a synthetic blue pigment (cerulean, ideally Co_2SnO_4 , a spinel with Co^{2+} ions in tetrahedral and octahedral coordination).



Results and discussion

Co *K*-edge XANES spectra are very similar for the studied porcelain samples. As expected from distinct oxygen environments – tetrahedral in $\text{Co Al}_2 \text{O}_4$, octahedral in $\text{Co}_2 \text{Si O}_4$ – the spectra collected from these double oxides containing exclusively Co^{2+} ions show similar details of steeply rising edges but display dissimilar edge-crest plus post-edge and pre-edge regions. Comparing the spectra collected from all model compounds, the influence of coordination geometry irrespective the formal valence of cobalt ions becomes apparent.

The first derivatives of normalized XANES spectra highlight the comparative variation of edge features, emphasizing the dominant effect of coordination environment of cobalt ion over its formal valence in the chemical formula of the compound.

Differences in pre-edge details obtained by deconvoluting the spectra with FITYK program [8] may be explained by the coordination geometry and local symmetry of cobalt ions, tetrahedral vs. octahedral, quite independently from the formal valence. Indeed, the absorption edge of *1s* XANES spectra from *3d* transition metals is due to electronic transitions from the *1s* core state to the *4p* conduction band, while pre-edge details arise from quadrupole transitions to *3d* empty states; in case the inherent inversion symmetry is broken (as for Co^{2+} , a high spin $3d^7$ ion with filled e_g and t_{2g} orbitals), local mixing of *3d-4p* wave functions allows for dipole transitions to occur, intensifying the pre-edge feature [9].

Comments and conclusions

Actual results are most timely because the relevance of interpreting the electronic behavior of cobalt largely overpasses the problematic of ancient blue glazes. Under the form of nanocrystalline thin films which magnetic behavior has been extensively studied, cobalt oxide-based materials have nowadays a great diversity of technological applications, ranging from heterogeneous catalysts to optical sensors and semiconductors.

Particularly, the present work clearly supports previously published considerations [10] on the questionable reliability of inferring a formal oxidation state for *3d* transition metal ions solely from XAFS data [9]. The fragility of such inference is clearly illustrated by a recent study [11] claiming the occurrence of cobalt ions in two formal valence states within the glaze of blue-and-white ancient Chinese porcelains: the poorly-defined “cobaltic oxide” Co_2O_3 [12,13] was used as model compound and the mean coordination number deduced by EXAFS analysis for Co^{3+} ions was lower than three – a value hardly explainable in view of the recognized structural array of silica-rich glazes. Indeed, the formal valence of a metal ion is strictly connected with the chemical formula of the carrier compound, while X-ray absorption data reflect the electron binding situation of the element, even if a specific chemical formulation cannot be stated (as is the case of amorphous phases like ceramic glazes).

Acknowledgements

Work developed under Project PTDC/HAH/69506/2006 financed by the Portuguese Foundation for Science and Technology (FCT-MCTES). The financial of EU to perform

XAFS experiments at the ESRF through the action Access to Research Infra-structures is acknowledged.

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