SPECIATION STATE OF COBALT IN BLUE GLAZES: A *XAFS* STUDY ON XVI CENT. CHINESE BLUE-&-WHITE PORCELAINS *

M.O. FIGUEIREDO [1,2], T.P. SILVA [1,2], J.P. VEIGA [2] & M.I. DIAS [3]

[1] Cryst. Miner. Centre, IICT & INETI/ IGM , Geol. Data Centre, Estrada da Portela, 2721-866 Alfragide,
[2] CENIMAT / I3N, Mater. Sci. Dept., Fac. Sci. & Technology, New Univ. Lisbon, 2829-516 Caparica,
[3] Nuclear & Technologic Institute (ITN), EN 10, 2686-953 Sacavém, Portugal

E-MRS EUROPEAN MATERIALS RESEARCH SOCIETY
SPRING MEETING
Strasbourg, June 8 -12
Symposium R
Poster 5 MS 9

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 sate 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 using synchrotron radiation*. The analysis of both near-edge features (XANES) and extended fine structure (EXAFS) has been extensively and successfully used to study chromophore ions or modifier elements in ancient glassy materials, namely tile glazes [e.g., 1-4].

The trade of Chinese blue-and-white porcelains to Europe became intense after the maritime contact first established by the Portuguese navigators by the end of XVI century. European museums and traders have now an increased need to ascertain the authenticity of such art objects through non-destructive assays. As a contribution, a XAFS study was undertaken to characterize cobalt speciation and coordination and tentatively date a set of fragments of Chinese porcelains (fig. 1) recovered during recent archaeological excavations conducted in Santa Clara-a-Velha Monastery (94, 95) at Coimbra, central Portugal [5] and in Lisbon Old-city (425, 426, 428). The results of such study are described and discussed.

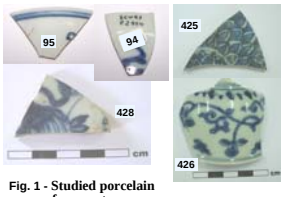
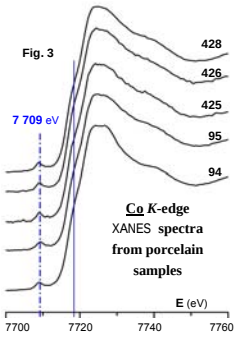
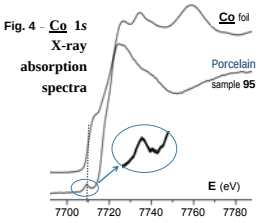


Fig. 1 - Studied porcelain fragments

Problematic

Ancient Chinese porcelain has been lately the object of many compositional studies applying X-ray and neutron analytical techniques to ascertain production periods and sites [6-8]. The reduced thickness of some archaeological shards hindered thermo-luminescence (TL) dating tests that could only be performed over Portuguese faience fragments collected at the same archaeological sites [9]. However, by visual appreciation it was possible to select for the present study Chinese shards (fig. 1) supposedly manufactured in the XVI cent. A.D. – that is, in the Ming period (1368-1644). Being known [10] that a shift from imported *arsenic-rich Persian cobalt pigments* towards *manganese-rich native Chinese blue pigmenting ores* has occurred during the *early Ming Dynasty* it is possible to use the As content plus a combination of Fe/Co & Mn/Co ratios as dating criterion [11].





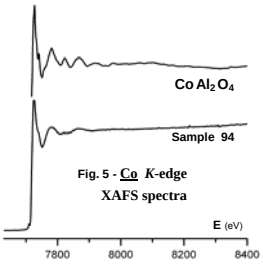


Fig. 2 – Instrumental set-up of beamline **BM-29**

Experimental

A *wavelength-dispersive X-ray fluorescence* (XRF-WDS) spectrometer Philips PW1400 with a rhodium tube and a LiF_{200} analysing crystal was used for the non-destructive bulk chemical study by irradiating the whole fragment in the case of smaller samples (94, 95, 428). Fixed-time counting was carried out over the *Kα* peaks of relevant transition metals - Mn, Fe, Co, Cu (Table 1); the presence of As was ascertained through *Kβ* peak whenever Pb was detected through the *Lα* peak.

Co 1*s X-ray absorption spectra* were collected using the instrumental set-up of beam line BM-29 at the ESRF in Grenoble/France (fig. 2) by directly irradiating the surface of glazed debris and detecting the fluorescence yield with a germanium detector. A cobalt metal foil was used to calibrate the energy. Double oxides with known crystal structure and commercial pigments (phase constitution previously checked by X-ray diffraction) were irradiated to model cobalt speciation and coordination environment.

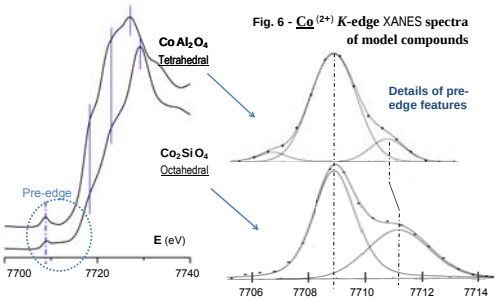


Fig. 6 - Co (2+) *K*-edge XANES spectra of model compounds

Results

Neither Pb nor As were detected by XRF-WDS and clearly distinct Mn/Co & Fe/Co ratios were obtained for thin (94-95-426) and thick (425-428) porcelain fragments (Table 1). Concerning Santa Clara-a-Velha, the present results agree with data from a recent μ-EDXRF study of a large set of porcelain shards carried out with a portable apparatus [12].

Collected Co *K*-edge XAFS spectra of glazes from all porcelain fragments (fig. 3) display the same general trend: an *intense pre-edge feature* at ~7709 eV (fig. 4), an edge energy indicative of a *divalent state* of cobalt ions (~7718 eV) and a *poorly detailed EXAFS region* (fig. 5).

Pre-edge features were resolved with Fityk program [13]. Slightly different details were obtained for Co^{2+} ions in tetrahedral and octahedral environments (fig. 6) and the quite intense pre-edge feature in the spectra of Chinese porcelains supports a tetrahedral environment around the $3d^7$ transition metal ion. Deconvolution of the EXAFS spectral region with a multiple scattering approach using IFEFFIT program [14] indeed validated a *mean coordination number between four and five* (figs. 7-8), thus confirming that cobalt plays the double role of blue chromophore (tetrahedral Co^{2+} ions [15]) and network-former (Co^{2+} ions with slightly higher coordination number) in the glassy matrix.

Table 1 – XRF-WDS data

Element	Sample (2θ°)	094 Santa Clara-a-Velha Monastery / Coimbra	095 Santa Clara-a-Velha Monastery / Coimbra	425 Lisbon Old-city (recent archaeological excavations)	426 Lisbon Old-city (recent archaeological excavations)	428 Lisbon Old-city (recent archaeological excavations)
background	71.00	360	314	123	112	190
Mn	62.97	14 376	22 229	8 557	4 524	47 638
Fe	57.52	102 270	104 162	9 836	27 001	67 388
Co	52.80	5 522	3 649	1 841	1 414	11 073
Cu	45.03	2 949	2 523	361	1 704	2 045
Mn/Co	–	2.6	6.1	4.6	3.2	4.3
Fe/Co	–	18.5	28.5	5.3	19.1	6.1

EXAFS ' fitting results

C N = 4.7 ± 0.6
Distance = ~2.0 Å
σ^2 = 0.010 ± 0.002 Å²
R (factor) = 0.0029
Reduced χ^2 = 7.8

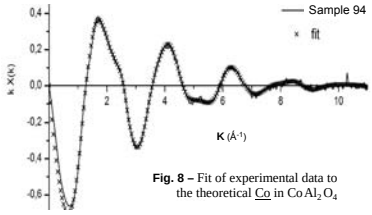
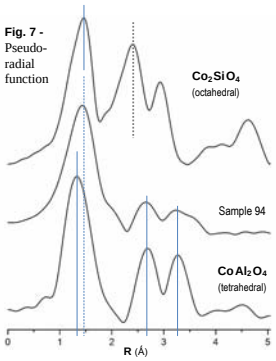


Fig. 8 – Fit of experimental data to the theoretical Co in $CoAl_2O_4$



Conclusions and comments

Chemical data – absence of arsenic and Mn-Fe-Co relative contents – corroborate an earlier dating for thicker samples (425, 428) and a later one for thin samples (94, 95, 426), as suggested by a previous artistic inspection – respectively, medium and late XVI century.

Differences in pre-edge features of spectra collected from model oxides (fig. 6) may be explained by the local symmetry of Co^{2+} ions: a regular tetrahedral coordination with the ideal site symmetry $\bar{4}3m$ in $CoAl_2O_4$ (spinel-type crystal structure) and octahedral coordination with two distorted site symmetries, ($\bar{1}$ and *m)* in Co_2SiO_4 (olivine-type structure).

Indeed, the absorption edge of 1*s* XANES spectra from 3*d* transition metals is due to electronic transitions from the 1*s* core state to the 4*p* conduction band, while pre-edge details arise from quadrupole transitions to 3*d* empty states; in case the inherent inversion symmetry is broken (as in the case of Co^{2+}, a high spin $3d^7$ ion with filled e_g and t_{2g} orbitals), local mixing of 3*d*4*p* wave functions allows for dipole transitions to occur, thus intensifying the pre-edge feature [16]. These comments fully explain the results obtained for both model compounds and porcelain samples.

References

[1] S. PADOVANI *et al.* (2004) Silver and copper nanoclusters in the lustre decoration of Italian Renaissance pottery: an EXAFS study. *Appl. Phys. A* 79 229.
[2] M.O. FIGUEIREDO *et al.* (2005) Chemistry versus phase constitution of yellow ancient tile glazes: a non-destructive insight through XAS. *Nuclear Instr. & Methods B* 238 134.
[3] M.O. FIGUEIREDO, T.P. SILVA & J.P. VEIGA (2006) A XANES study on the structural role of lead in glazes from decorated tiles, XVI to XVIII century manufacture. *Appl. Phys. A* 83 209.
[4] J.P. VEIGA & M.O. FIGUEIREDO (2008) A XANES study on the structural role of zinc in ancient tile glazes. *X-ray Spectrometry* 37 458.
[5] C.P. SANTOS (2003) Chinese porcelain of Santa Clara-a-Velha, Coimbra: fragments of a collection. *Oriental Art* 49 3.
[6] P.L. LEUNG & H. LUO (2000) A study of provenance and dating of ancient Chinese porcelain by X-ray fluorescence spectrometry. *X-ray Spectr.* 29 34.
[7] H.S. CHENG *et al.* (2002) Non-destructive analysis and appraisal of ancient Chinese porcelain by PIXE. *Nuclear Instr. & Methods B* 190 488.
[8] R. WEN *et al.* (2007) The chemical composition of blue pigment on Chinese blue-and-white porcelain of the Yuan and Ming Dynasties (1271-1644). *Archaeometry* 49 101.
[9] M.I. DIAS *et al.* (2008) Materials and pigments from Portuguese faience in the XVII-1st half of the XVIII century. *37th Int. Symp. on Archaeometry, ISA 2008*, Siena / Italy (poster).
[10] H. GARNER (1956) The use of imported and native cobalt in Chinese blue-&-white. *Oriental Art* 2 48.
[11] H.S. CHENG et al. (2002) Some new results of PIXE study on Chinese ancient porcelain. *Nuclear Instr. & Methods B* 240 527.
[12] M. LARSSON & J.P. VEIGA (2008) Ming porcelain from Santa Clara-a-Velha Monastery in Coimbra, Portugal. First results using a portable μ-EDXRF spectrometer. In *Geoarch. and Archaeominer.*, Proceedings Internat. Conf., Publ. House St. Ivan Rilski, Sofia/Bulgaria, 134.
[13] http://www.unipress.waw.pl/fityk
[14] M. NEWVILLE (2001) IFEFFIT: interactive XAFS analysis and FEFF fitting. *J. Synchr. Radiation* 8 322.
[15] A.L. FERNANDÉZ & L. de PABLO (2002) Formation and the colour development in cobalt spinel pigments. *Pigment & Resin Technol.* 31 350.
[16] F. de GROOT, G. VANKÓ & P. GLATZEL (2009) The 1s X-ray absorption pre-edge structures in transition metal oxides. *J. Phys. Condensed Matter* 21 (7 pp.)

* Work developed under Project PTDC/HAH/69506/2006 financed by the Portuguese Foundation for Science and Technology (FCT-MCTES). EU financial support to perform the experiments at the ESRF through the action Access to Research Infra-structures is acknowledged.