Inferring the formal oxidation state of 3*d* metal ions from *K*-edge XANES spectra: how far can we go for cobalt in ancient Chinese porcelain glazes?

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The relevance of interpreting the electronic behaviour of cobalt largely overpasses the problematic of ancient blue glazes, from either ceramics or porcelains. Under the form of nanocrystalline thin films which magnetic behaviour has been extensively studied [1], cobalt oxide-based materials have nowadays a great diversity of technological applications, ranging from heterogeneous catalysts [2] to optical sensors and semiconductors [3].

Archaeological findings of Chinese porcelains are important potential contributions to set up dating processes. In fact, the composition of cobalt blue pigments used in ancient Chinese glazes is known to have changed between the 14th and the 17th century and ratios of some main chemical components plus trace elements are relevant guide-lines to establish the porcelain manufacture period. The speciation state of cobalt in blue-and-white glazes from Chinese porcelain fragments supposedly dated from the 16th-17th century was recently addressed through an X-ray absorption near-edge (XANES) study performed at the Co *K*-edge [4], following a preliminary extended X-ray absorption fine-structure (EXAFS) study having revealed a coordination of cobalt ions slightly above four. Pre-edge details and edge features were analysed by comparison with spectra collected from model compounds with well known crystal structure and formal valences of cobalt ions – Co_3O_4, $CoAl_2O_4$ and Co_2SiO_4, plus a cobalt-based blue pigment (cerulean, ideally Co_2SnO_4). Obtained chemical data validated the manufacture period and, contrary to previous suggestions about the occurrence of two oxidation states for cobalt ions [5], actual XANES results confirmed a coordination environment of blue pigmenting Co^{2+} ions close to tetrahedral and sustain the dual role of cobalt as network former plus modifier in the glaze of ancient Chinese porcelains.

Due to the complexity of the electronic structure of 3*d* transition elements, the energy position of the absorption edge was recently questioned as a consistent criterion to infer the oxidation state of those elements [6], a query that the present spectroscopic study clearly supports.

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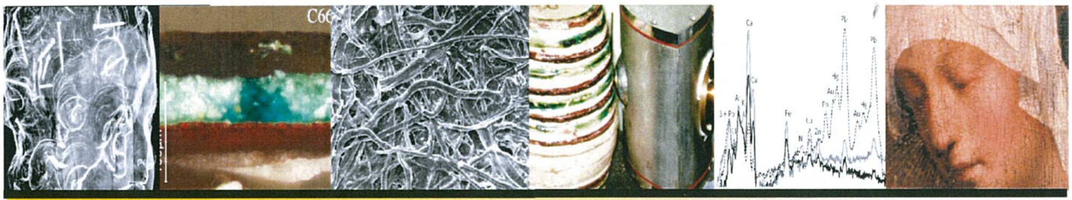

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