Supplementary information

XANES analysis

The X-ray Absorption Near Edge Structure (XANES) analysis was performed at the Co K-edge to obtain information on the Co oxidation state and on the geometry of the Co site in the different pigments. Fig. 1supp. reports the XANES spectra of the fresh smalt (A0) and of the altered specimen from the original banner (S3). From the comparison of the two experimental spectra, it is possible to establish the valence state of Co deduced by the energy position of the absorption K-edge. For both samples, the Co K-edge is located at about 7717 eV, in agreement with the energy position of CoO used as standard for the Co^{2+} oxidation state. It is worth noting that the edge energy for $Co(C_5H_7O_2)_3$, i.e. Co(III) standard compound, is shifted to higher energy (~ 7724 eV) [1]. Furthermore, the presence of a strong pre-edge peak and a smooth white line are typical of a non centrosymmetric structure, as is the tetrahedral one; whereas a reduced intensity of a pre-edge peak and a more pronounced white line is an indication of an octahedral symmetry [1, 2]. This is confirmed by the theoretical XANES spectra [3], calculated for tetrahedral CoO_4 and octahedral CoO_6 complexes with bond distances derived from the EXAFS results, and reported in the top-right inset of Fig. 1

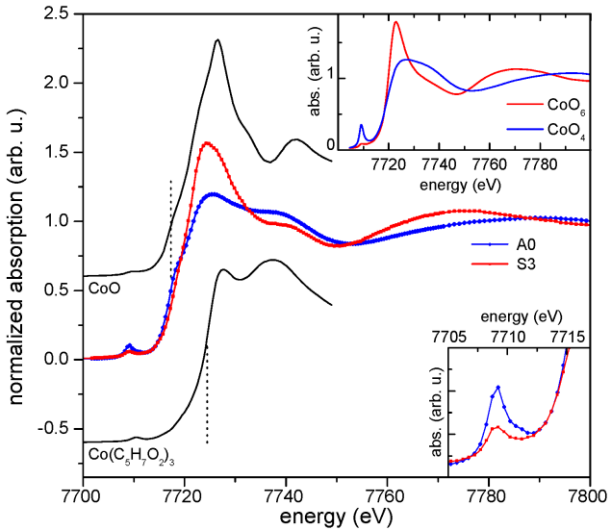

Fig. 1 Experimental XANES spectra of the fresh smalt (blue line with markers) and of the deteriorated sample (red line with markers), compared with spectra of reference compounds CoO and $Co(C_5H_7O_2)_3$ containing solely Co(II) and Co(III) respectively. The edge position is marked by the dashed line. Upon deterioration a decrease of the pre-edge peak at 7709 eV and an increase of the white line at 7722 eV are evident. An enlarged view of the pre-edge region is presented in the inset at the low-right side. These same features are found in the comparison between the theoretical XANES spectra of octahedral CoO_6 and tetrahedral CoO_4 complexes (inset in the top-right side). XANES calculations were carried out based on Co-O distances taken from the EXAFS analysis (R_{tet} = 1.95 Å R_{oct} = 2.14 Å).

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[2] M. Benfatto, C. R. Natoli, A. Bianconi, J. Garcia, A. Marcelli, M. Fanfoni, and I. Davoli, Phys. Rev. B 34, 5774 (1986).

[3] Y. Joly, Phys. Rev. B 63, 125120 (2001).