ESRF	**Experiment title:** Study of Sn/Pb oxydation state in opacifiers precursors used in medieval enamels	**Experiment number**: **08-01-953**
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Report:

Local atomic environment around tin and lead of eight bulks soda-lime enamels has been investigated. The aim of the experiment was to check the possibility to discriminate the crystalline origin of medieval enamels observing the metal coordination evolution of tin and lead within the glass matrix [1, 2].

Working at 80 K, standard XANES and EXAFS data at L_3-Pb edge and at K-Sn edge were collected in transmission mode, using an ion chamber filled with argon and normalized by measuring the incident beam with an ion chamber filled with argon gas.

The XAS signals were extracted with the ATHENA code and quantitative analysis was carried out with the ARTEMIS program using theoretical Extended X-ray Absorption Fine Structure (EXAFS) paths calculated with the Feff6 code. We employed a smoothing spline algorithm to reproduce μ_0 and choosed the energy edge value (E_0) at the maximum of the derivative. The free-fitting parameters used in the analysis are: S^2_0 (common amplitude parameter), ΔE_0 (the refinement of edge position), R and σ^2, the interatomic distance, and the Debye-Waller factor for the first atomic shell around the absorber. The fit is carried out in the

Fourier-transformed space (R space) from the K^2-weighted EXAFS data using Hanning windows with slope-parameter dk=1 and dR=0.5, for the forward and backward Fourier transforms, respectively.

The XANES analysis performed at L_3-Pb edge shows that all the samples have similar valence state of the lead in PbO (see Fig. 1); indeed no components related to PbO_2 were found (see Fig 2).
The EXAFS oscillations in the K range are not very intense and soften rapidly after the edge. We can then affirm that local disorder is present around the Pb atoms. The analysis of first shell was carried out (see Fig. 1) and the data are collected in the Table 1. The distance between Pb and O are reported.

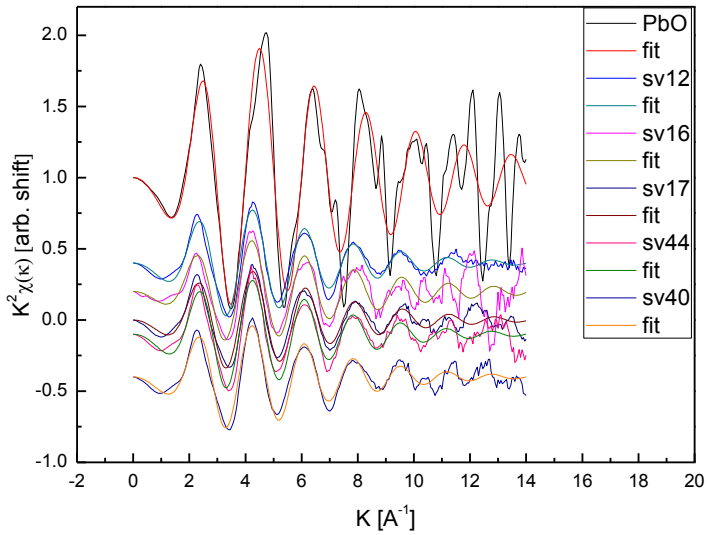

Fig1: EXAFS spectra, acquired at L3 Pb edge, recorded from the samples with their corresponding fits.

Sample	ΔE_0 (eV)	S_0^2	r_{Pb-O} (Å)	σ^2 (Å^2)	R_{factor}
PbO	-2.5 ± 0.6	1.06 ± 0.08	2.147 ± 0.007	0.003 ± 0.001	0.0009
SV12	-0.9 ± 0.9	0.58 ± 0.06	2.252 ± 0.012	0.007 ± 0.002	0.003
SV16	-2.7 ± 1.1	0.52 ± 0.06	2.239 ± 0.014	0.005 ± 0.002	0.004
SV17	-1.8 ± 1.0	0.52 ± 0.06	2.237 ± 0.012	0.007 ± 0.002	0.003
SV40	-0.4 ± 0.7	0.59 ± 0.05	2.256 ± 0.010	0.007 ± 0.002	0.002
SV44	-1.1 ± 0.7	0.56 ± 0.05	2.254 ± 0.010	0.007 ± 0.002	0.002

Table1: results of the quantitative analysis of the first shell performed on the EXAFS data.

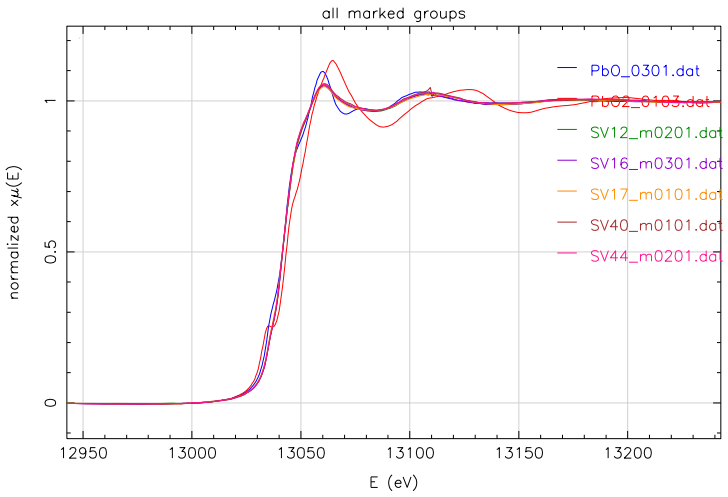

Fig 2: spectra, acquired at the L3-Pb edge, reported at the XANES region of the samples and references.

The XANES analysis performed at K-Sn edge, shows that all the samples have valences far from the SnO reference but coherent with the SnO_2 reference.

The EXAFS data were fitted with this model and it is possible to perform a fit up to R = 6 Å (see fig 3). This means that a crystalline order is presents around Sn atoms. Probably Sn crystalline clusters inside the glass are present.

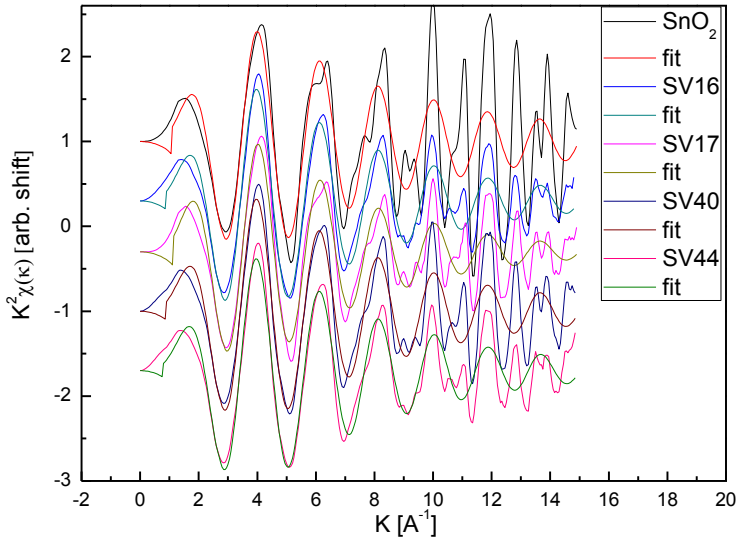

Fig 3: EXAFS spectra, acquired at K Sn edge, recorded from the samples with their corresponding fits.

In conclusion, at the end of this first analysis, we can conclude that the experiment carried out at the Italian beamline GILDA at ESRF was successfully performed. The EXAFS analysis shows that the Sn atoms are surrounded by an oxygen network in an ordinated crystalline lattice. This is in accord with the clusterization of SnO_2 (cassiterite) during the opacifying process (see fig. 4).

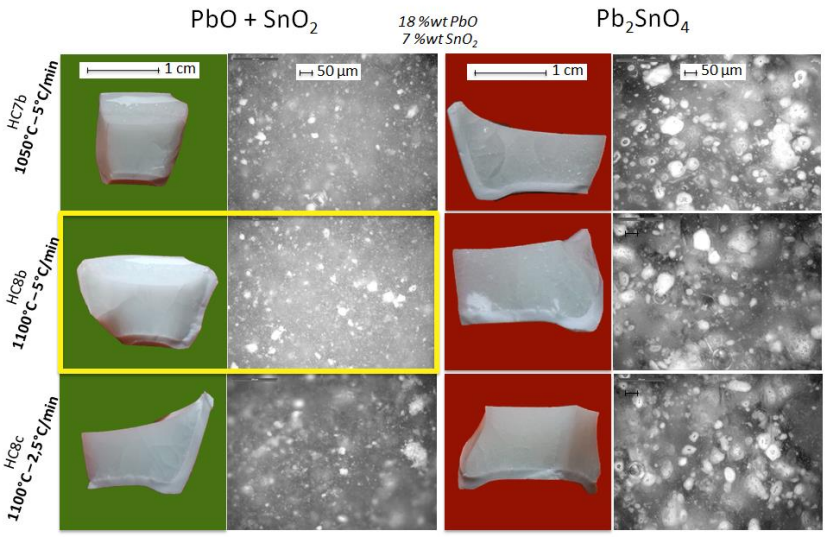

Fig 4: Selected enamel samples accompanied with optical microscope pictures.

Different results can be related to the lead, that, due to its short range organized network, is scattered in the glass matrix, as well as the former (SiO_2). The resulting coordination is indeed unusual because this ion is surrounded by three oxygen in the first shell.

Nevertheless we have observed that samples, prepared with different protocols, present similar coordination and electronic structure. This will make more complicated any effort to link samples specific properties to specific crystalline origin. This link could be pointed out only after a careful multiple shell analysis of the signal.

Acknowledgements:

We thank all the staff of ID08 for the support.

References:

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2. Tite, M., Pradell, T., & Shortland, A. (2008). Discovery, production and use of tin-based opacifiers in glasses, enamels and glazes from the late iron age onwards: A Reassessment, Archaeometry, 50, 1 (2008) 67–84