

XANES and Mössbauer study of the oxidation state of ancient glass

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The evaluation of the oxidation state of coloring elements in ancient glass offers important information not only about color, but also on the technology of the ancient glassmakers. Concerning iron, few information is published on the relative $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios. In fact, this type of measurements is challenging, due to the low $\sum\text{Fe}$ contents of the glasses, typically in the range 0.3 – 1.0%.

We have combined Mössbauer and XANES measurements to study a selected series of ancient glasses - mainly from excavated primary and secondary production centers and dated to the first millennium AD - which provide a wide range of iron compositions. In addition, some of the samples were chosen to determine the differences in the relative Fe oxidation state in closely related glasses from a single production sequence.

Good agreement between the two techniques was obtained for the more oxidized glasses ($\text{Fe}^{3+} > 60\%$), while some significant differences are evident in the more reduced samples, with XANES generally suggesting higher Fe^{3+} content. The results on the decolorized glass indicate that Sb is more effective than Mn in oxidizing iron. Primary natron glass from an early Islamic tank furnace at Bet Eli'ezer (Israel), shows a high level of Fe^{3+} in the bluish glasses, but greenish/olive samples - of essentially the same composition - appear less oxidized and hence originated in regions of the furnace with less access to air. Conditions in a primary furnace producing amber glass were rather reducing. A sequence of moils from a glass working furnace in London demonstrates progressive oxidation of the melt as the working campaign progressed. Iron in strongly colored fourth century HIMT glass is very oxidized, due to the high content of Mn; the strong color of these samples is due to their high iron content, but Fe^{3+} is more-or-less constant irrespective of the total amount of iron present. Primary chunk soda ash glass from the tank furnaces at Tyre (Lebanon), has an intermediate oxidation state, while a chunk from Banias (Israel) is fully oxidized, although manganese oxide has been added in both cases to oxidize and decolor the glass.