Characterization of the radiation damage of ultramarine pigments by microscale x-ray spectroscopy

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As one of the most desired and expensive artists' materials throughout history, there has long been interest in determining the chemistry responsible for the blue hue of the ultramarine pigment. In particular sulfur K-edge XANES has been particularly suited to determine the chemistry of the sulfur species identified as the first color center of the pigment.

Although its interpretation is complicated by the complexity of overlapping species in the XANES spectra, two of the major characteristic features have been described in the literature as: (i) a distinctive pre-edge feature, centered at 2469 eV, assigned to the S_3^- polysulfide radical anion, considered as the blue chromophore, and (ii) a series of reduced sulfur radicals (S_2^-, S_3^-, S_4^-) and elemental sulfur (S_8) resulting in a broad absorption envelope between 2470 and 2475 eV.

The potential lability of the sulfur radicals has motivated this research to assess the effect of possible radiation damage to S-based species, in order to define the optimal acquisition parameters to allow safe analyses of ultramarine pigments. Radiation damage tests were carried out using unfocused and focused beams on raw lapis lazuli rock materials and three different grades of extracted pigments. Statistical analyses show that the radiation damage creates a loss of the S-S bonds of the polysulfides/S_8 species, and an increase of the S_3^- radical blue centers and thio-sulfides, providing initial insights into the photo-induced reaction. Calculation of the dose applied to the sample allows a kinetic analysis of the reaction, showing that the induced damage follows first-order kinetics with respect to the polysulfide/S_8 species. These results show the high reactivity of the polysuflide and sulfur radical species in the x-ray beam and allow a first assesment on the acceptable amount of radiaiton exposure. Further work will continue to assess the reactivity in the complex matrices found in real-life Cultural Heritage materials.